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Unit processes i

CHEMICAL ENGINEERING SERIES

UNIT PROCESSES IN ORGANIC SYNTHESIS

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CHEMICAL ENGINEERING SERIES

UNIT PROCESSES IN ORGANIC SYNTHESIS

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Unit processes i

PREFACE TO THE THIRD EDITION

In the preface to the first edition, the editor distinguished between the now established terms *unit processes* and *unit operations* and showed how they were intimately related in the solution of chemical engineering problems involving organic synthesis. The objective of the present volume continues to be the presentation of the industrial technic employed in attacking problems of organic synthesis. Accordingly, the underlying principles and factors for each unit process are organized in a systematic manner with particular emphasis on the industrial and economic importance of individual syntheses.

During recent years, foreign sales of "Unit Processes" have almost equaled domestic distribution. This is merely a reflection of the enormous growth of the synthetic organic chemical industry in other parts of the world. There is every indication that this trend will continue, not only in the United States but particularly in the industrially more backward nations and colonies. This remarkable growth of the chemical industry will in all probability be accompanied by a considerable domestic decentralization as well as international migration of chemical plants. This stems largely from the fact that petroleum and natural gas have displaced coal as the principal source of basic chemicals for organic syntheses. Indeed, many important intermediates, such as toluene, xylenes, and cresols, that heretofore were obtained exclusively from coal tar are being produced or obtained in large volume from petroleum. The production of butadiene and polyisobutylene for the synthetic rubber program are based on petroleum, while considerable quantities of acetaldehyde and acetic acid are derived from natural gas. It is also noteworthy that natural gas is the most economic hydrocarbon for the Fischer-Tropsch process and for the production of synthetic ammonia. This may have an impact on the established manufacture of numerous organic compounds such as methanol, formaldehyde, glycolic acid, hydrocyanic acid, and urea that can be synthesized in a water-gas ammonia plant.

In this third enlarged edition, the general plan of the book remains unchanged, but every chapter has been extensively revised and brought into line with current developments as revealed by the technical and patent literature. Mention should be made of (1) the greatly increased emphasis on the synthesis of aliphatic compounds, (2) the incorporation of many new flow diagrams, and (3) the introduction of an appendix containing charts showing the diverse products that can be obtained from petroleum hydrocarbons and of numerous tables giving chemical properties and physical constants of a large number of the compounds discussed in the text.

The chapter on Polymerization has been completely rewritten by Professors Mark and Howenstein. Dr. Mark has for many years been recognized as one of our foremost authorities in the field of high polymers. The new contribution should prove useful in presenting or reviewing the fundamental principles of this unit process.

The editor is again deeply obligated to many of the leaders in the chemical industry who have reviewed chapters and made constructive criticisms and suggestions. By way of compensation, it is hoped that their cooperation and contributions will result in a better training of chemists and chemical engineers for their plants.

P. H. GROGGINS

WASHINGTON, D. C.,
January, 1947.

PREFACE TO THE FIRST EDITION

During the past half century, the activities of workers in the field of organic synthesis have swelled to unwieldy proportions our store of information regarding new products. As a result thereof, most organic chemists have been constrained to focus their interest to some restricted field. Beyond his immediate professional problems, the chemist is generally not so much interested in the countless new carbon compounds that are synthesized as he is in the reaction mechanism and technic employed. To derive the fullest benefit from the accumulated knowledge and current contributions, it is obviously advantageous to record the development of organic synthesis in terms of the comparatively few underlying unit processes.

In this book, an attempt is made to present in a systematic manner the principles and practice of the more important and well-defined reactions in organic synthesis. In commercial operations, it is found necessary to bring to the application of such reactions the pertinent information derived from inorganic and physical chemistry as well as the contributions of the chemical engineer. Hence, attention is directed not only to the chemistry and products of reaction but equally to the contributing factors and agencies that lead to efficient operation. The term *unit processes* is used here to represent the embodiment of all the factors in the technical application of an individual reaction in organic synthesis.

The desirability of employing such a concise and descriptive term can be appreciated readily from the following illustration: In the process of synthesizing dimethylaniline from benzene, three distinct unit processes are involved, *viz.*, (1) nitration; (2) amination by reduction; and (3) alkylation. Similarly, in each of the two current methods of synthesizing phenol from benzene, two unit processes are required; thus: (1) sulfonation followed by hydrolysis or (2) halogenation followed by hydrolysis.

Perhaps a few words of explanation are warranted here to distinguish between the term *unit process* as we have used it and the term *unit operation*, which now has a definite significance to the chemical engineer. Unit processes deal principally with chemical reactions, whereas unit operations relate largely to physical phenomena. The former are based on changes in chemical constitution or molecular structure; the latter involve changes of state or position. Unit processes bring about distinctive chemical transformations in the materials treated, these changes being conditioned largely by the intrinsic properties of the reactants.

On the other hand, the factors affecting physical movements or changes, *i.e.*, the underlying principles of unit operations, may in many instances be discussed apart from the chemical nature of the materials handled.

Unit processes and unit operations have, however, important interrelations, for no reaction or series of reactions can be carried out commercially without the application of one or more unit operations. Thus, in nitration, some of the unit operations that are involved are conveying and feeding material; mixing; heat transfer; separation of materials; filtration; and distillation. In this volume, however, the authors have assumed that the reader is familiar with the principles of the chemical engineering unit operations, which are competently discussed in other texts of this series. A knowledge of these is essential to the technical application of chemical engineering to unit processes in organic synthesis.

Examination of the literature relating to any unit process in organic synthesis reveals that there may be many means to the same end. In this work, an effort is made to codify the underlying principles and factors, for the satisfactory interpretation of any unit process depends on discovering the common among the apparently diverse reactions. The formulation of a practical philosophy of each reaction should consequently include (1) an examination of the reactants; (2) an inquiry into the mechanism of the reaction; (3) a knowledge of the chemical and physical factors involved; (4) observations regarding the design and construction of equipment; and, finally, (5) a study of typical technical applications. Once the principles are mastered, it matters little in what branch of chemical technology these processes are carried out.

This volume is therefore intended for advanced students in chemistry and chemical engineering. An attempt has been made to coordinate the study of fundamental principles of organic synthesis with the requirements of the industrial plant. The text may be viewed as a semiworks course to facilitate the transition from the classroom to the works laboratory.

To amass, digest, and interpret the literature of each unit process was recognized as a task calling for specialized experience. To assure the practicability and reliability of the text, it has been considered essential to make the work a collaborative effort. In addition, individual chapters have been sent to industries and universities for critical examination, and the able and valuable assistance given by members of such organizations and institutions is hereby gratefully acknowledged.

WASHINGTON, D. C.,
November, 1934.

P. H. GROGGINS,

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UNIT PROCESSES IN ORGANIC SYNTHESIS

CHAPTER I

NITRATION

By P. H. Groggins

Nitration may be considered as the process by which the union of the nitro (—NO_2) group to a carbon atom is effected. Generally, it is the hydrogen atom that is replaced; thus,

$$R{\cdot}H + HO{\cdot}NO_2 \rightarrow R{\cdot}NO_2 + H{\cdot}OH$$

Although a number of methods for the preparation of nitro compounds are available, the nitro group is usually introduced by the action of nitric acid admixed with some other acid that preferentially combines with the water in the reaction system. The comparative ease with which nitration occurs in the presence of such dehydrating agents has led to the belief that nitration is probably due to the activity of either nitric acid anhydride or mixed acid anhydrides. These compounds possess pronounced additive properties and contain a labile —NO_2 group, *e.g.*, $O_2N{\cdot}O{\cdot}NO_2$, $H_3C{\cdot}CO{\cdot}O{\cdot}NO_2$. Generally, however, the representation of the reaction involves the union of the hydrogen that is replaced with the hydroxyl of nitric acid to form water.

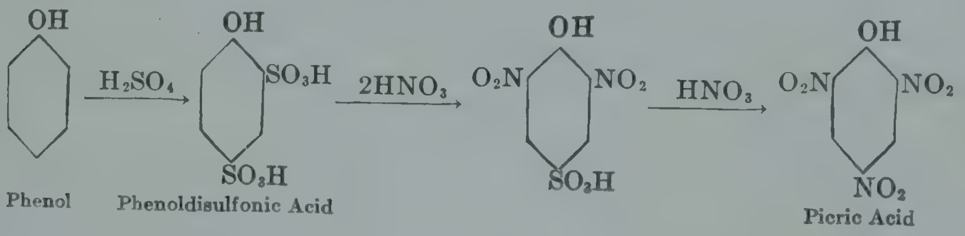
The agents generally employed for the preparation of nitro compounds are the following:

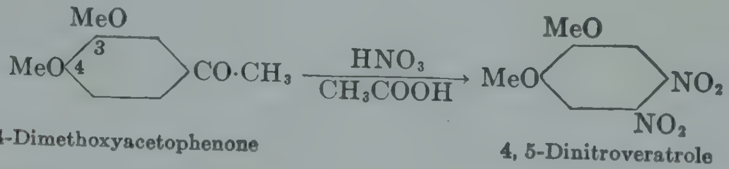
1. Nitric acid, concentrated and dilute, liquid and vapor.
2. Mixed acids, *i.e.*, nitric acid admixed with a dehydrating acid such as oleum, sulfuric acid, acetic anhydride, acetic acid, phosphorus pentoxide.
3. Alkali nitrates in the presence of sulfuric acid.
4. Organic nitrates, such as acetyl and benzoyl nitrates.
5. Metal nitrates with acetic acid.
6. Nitrogen tetroxide.

It is apparent from the preceding tabulation of nitrating agents that the nitro group can be introduced by various procedures. The choice of agent and the technic employed will be governed by such factors as the chemical constitution and physical properties of the organic compound as well as by the economics of competitive methods. Such variations in any unit process are instructive and to be expected.

A parallelism exists in other unit processes. In the preparation of amino compounds, a wide variety of aminating agents are available. Thus, NH_3 *aq.*, NH_3 (in organic solvents), $(NH_2)_2{\cdot}CO$, $R{\cdot}SO_2{\cdot}NH_2$, etc., may be effectively employed. The satisfactory interpretation of any unit process obviously depends on discovering the common among the apparently heterogeneous reactions.

In a few cases, not a hydrogen atom but another group, such as the sulfonic acid ($—SO_3H$) or acetyl ($—COCH_3$) group, is replaced. Examples of interest are the nitration of phenoldisulfonic acid, which is thereby converted into picric acid; and the nitration of 3, 4-dimethoxyacetophenone in glacial acetic acid to 4, 5-dinitroveratrole.


OH
H₂SO₄
OH
SO₃H
SO₃H
2HNO₃
OH
O₂N
NO₂
SO₃H
HNO₃
OH
O₂N
NO₂
NO₂
Phenol
Phenoldisulfonic Acid
Picric Acid


MeO
MeO
3
4
CO·CH₃
HNO₃
CH₃COOH
MeO
MeO
NO₂
NO₂
3, 4-Dimethoxyacetophenone
4, 5-Dinitroveratrole

It is possible to replace more than one hydrogen atom by nitro groups; and in this way, dinitro and trinitro compounds may be formed. The preparation of mononitro compounds is comparatively easy. It is more difficult, however, to bring about the introduction of the second and third nitro groups. In the last case, it is necessary to use an excess of mixed acid containing a high nitric acid concentration and to nitrate at higher temperatures.

I. SURVEY OF NITRO COMPOUNDS

The Nitroparaffins.—The comercial production of nitroparaffins by the continuous nitration of paraffins in the vapor phase, which was initiated in 1940, has not only introduced another group of interesting and highly reactive compounds but also opened up a new field of organic chemistry.[1] The raw materials for the preparation of the nitroparaffins are natural gas and petroleum, which are available in practically unlimited quantities, and cheap nitric acid or nitrogen dioxide derived from the oxidation of synthetic ammonia.

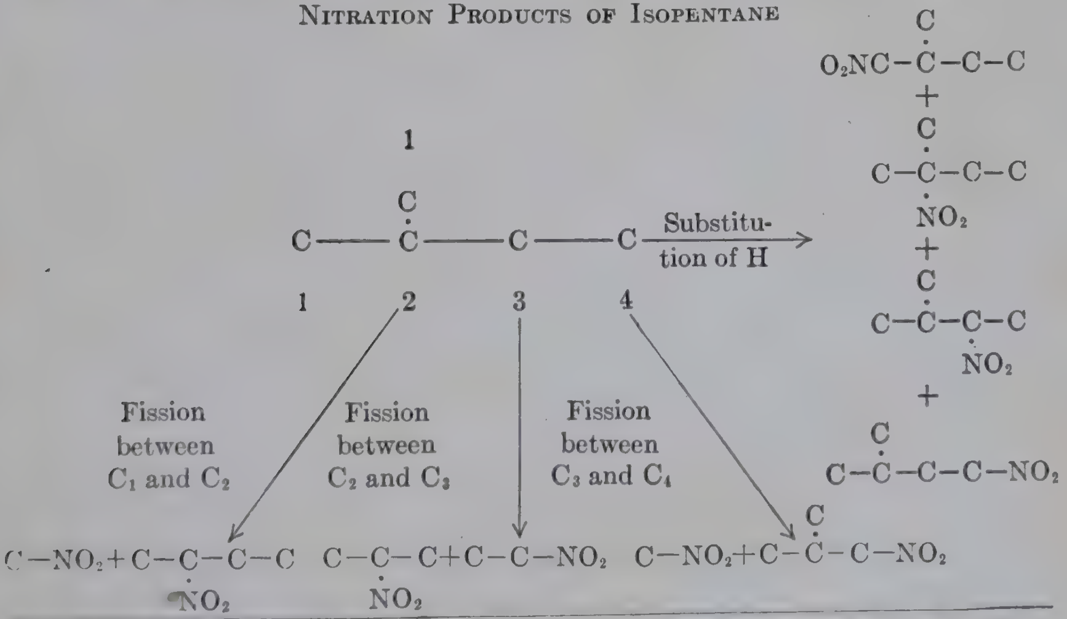
---

[1] Credit for this outstanding development is due Prof. H. B. Hass and coworkers at Purdue University. Although a considerable technical and patent literature on the subject has rapidly emerged, the following references are suggested: Hass and Hodge, U. S. 1,969,667 (1934); Hass, Hodge, and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936); Hass and Patterson, *Ind. Eng. Chem.*, **30**, 67 (1938); McCleary and

The nitration of paraffins introduces a new technic that is a marked departure from the familiar method of nitration with mixed acid which is used in the treatment of aromatic compounds. Whereas low temperatures (0 to 100°C.) and high acid concentrations are advantageously employed for the nitration of aromatic compounds, carbohydrates, and polyhydric alcohols, the most favorable conditions for nitrating the lower paraffins in the vapor phase are provided by using high temperatures (350 to 500°C.) and relatively dilute nitric acid. The sulfuric-nitric acid mixture used for nitrating aromatic hydrocarbons in the liquid phase is not suitable for paraffins. Primary nitroparaffins are quickly hydrolyzed by hot sulfuric acid, and the secondary and tertiary isomers are converted to brown tars.

When a paraffin is nitrated in the vapor phase at 350 to 500°C., all of the mononitrosubstitution products are obtained that could result if we conceive of the nitro group as capable of substituting either any hydrogen or any alkyl radical present. Thus, 2-methylbutane (isopentane) yields 1-nitro-2-methylbutane, 2-nitro-2-methylbutane, 3-nitro-2-methylbutane, and 4-nitro-2-methylbutane by substituting any one of the various hydrogen atoms, and it yields nitromethane, nitroethane, 2-nitropropane, 2-nitrobutane, and 1-nitro-2-methylpropane by substituting alkyl groups.

NITRATION PRODUCTS OF ISOPENTANE


1
1
2
3
4
Substitution of H
Fission between C₁ and C₂
Fission between C₂ and C₃
Fission between C₃ and C₄

DEGERING, *Ind. Eng. Chem.*, **30**, 64 (1938); VANDERBILT and HASS, *Ind. Eng. Chem.*, **32**, 34 (1940); HASS, *Ind. Eng. Chem.*, **35**, 1146 (1943); HASS and RILEY, *Chem. Rev.*, **32**, 373 (1943); Hass *et al.*, U. S. 2,071,122 (1936); U. S. 2,161,475 (1939); Hodge, U. S. Reissue 21,658 (1940); Martin and Hodge, U. S. Reissue 21,657 (1940); Martin, U. S. 2,260,258 (1941).

The vapor-phase nitration of the lower paraffins at temperatures in excess of 250°C. does not yield dinitroparaffins with either nitric acid or nitrogen dioxide as nitrating agent. The effect of increased temperature is to increase (1) the velocity of reaction, (2) the production of primary nitroparaffins at the expense of secondary and tertiary isomers, and (3) the yield of fission products. Conversions are constant over a wide temperature area when exposure time and temperature are carefully matched. When conversion is plotted against temperature at constant exposure time, a curve is obtained that rises, passes through a maximum, and declines. Temperatures below the optimum are too low for completion of the reaction; those higher than the optimum result in extensive pyrolysis of the nitroparaffins. The importance of this phenomenon is recognized in the commercial nitration of propane where the temperature is controlled to within ±1°F.

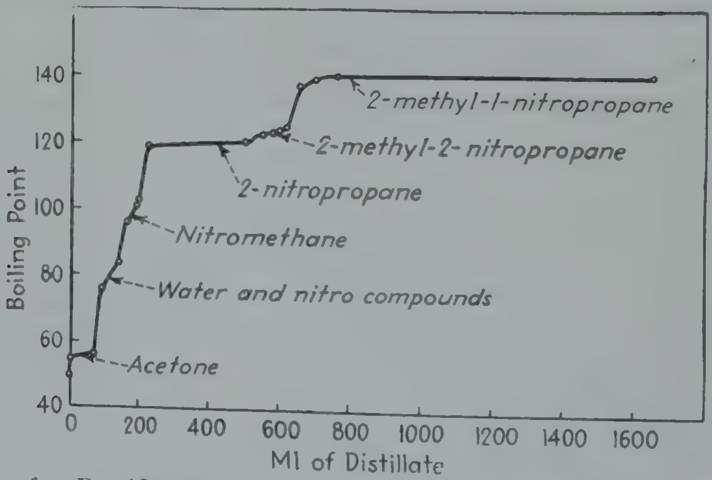


FIG. 1.—Rectification curve: products from nitration of isobutane.

The effect of pressure is to increase greatly the rate of reaction without usually affecting the conversion to a large extent. When the reaction chamber is made of stainless steel instead of glass or fused silica, conversions decrease, presumably on account of the formation of a film of metallic oxides. The adverse effect of this film can be eliminated by the continuous introduction of a small quantity of sodium or potassium nitrate into the reactor.[1]

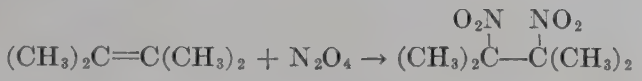
Under favorable conditions, approximately 40 per cent of the nitric acid passed through the reactor forms nitroparaffins which are separated by rectification (Fig. 1). The remainder functions as an oxidizing agent, being reduced almost exclusively to nitric oxide. Alcohols, carboxylic acids, aldehydes, ketones, carbon oxides, and water are thus formed in various quantities. In commercial practice the nitration is carried out in a continuous manner, and the nitric oxide is separated from other reaction

[1] U. S. 2,260,258 (1941).

products (see technical section) and excess of unchanged hydrocarbon and is reoxidized to nitric acid. Thus eventually more than 90 moles of nitroparaffins can be produced for each 100 moles of nitric acid consumed.

A study of the ratio paraffin to nitric acid shows that complete conversion at infinite ratio is not obtainable. Oxidation accompanies and does not merely follow the nitration reaction; *i.e.*, the nitric acid and oxides of nitrogen oxidize the hydrocarbon as well as the nitroparaffin.

Preparation of Nitroparaffins in the Liquid Phase.—Certain olefins add nitrogen tetroxide to yield dinitroparaffins. Thus, 2, 3-dimethyl-2-butene reacts as follows:



$$(CH_3)_2C{=}C(CH_3)_2 + N_2O_4 \rightarrow (CH_3)_2\overset{O_2N}{\overset{|}{C}}{-}\overset{NO_2}{\overset{|}{C}}(CH_3)_2$$

Tetrachloro- and tetrabromoethylene react analogously to yield 1, 2-dinitrotetrahalogenoethanes. When a diolefin such as butadiene is treated with two volumes of nitrogen dioxide in the presence of carbon dioxide, a dinitrobutylene is obtained in the form of a fluid oil. By recrystallization from ether, yellow crystals—which change to an unstable oil at room temperature—are obtained.[1]

The experimental work pertaining to the liquid-phase nitration of paraffins with nitric acid may be summarized as follows:

1. Reaction is slow, but yields and conversions are increased at higher temperatures.
2. Oxidation accompanies nitration, and the bulk of the nitric acid is reduced to elementary nitrogen—which prevents recovery by reoxidation—and thus constitutes an economic barrier to the industrialization of such operations.
3. Polynitro compounds are formed, attributable to the solubility of the nitroparaffin in the nitrating acid, where it is oxidized, nitrated, and hydrolyzed.
4. The sulfuric-nitric acid mixture, generally used for the nitration of aromatic hydrocarbons, is not suitable for the treatment of paraffins. The primary nitroparaffins are quickly hydrolyzed by hot sulfuric acids, and the secondary and tertiary isomers are converted to brown tars.

Liquid-vapor-phase Nitration of Higher Paraffins.—When higher paraffins in the liquid phase are nitrated with nitric acid in the vapor phase, the reaction proceeds smoothly at relatively low temperatures.[2] Mixing of the reactants is accomplished in a simple and efficient manner by feeding the nitric acid through a coil submerged in the paraffin undergoing reaction. The hydrocarbon is maintained above 121°, the maximum boiling point of nitric acid of 65.70 per cent strength, while the incoming vaporized acid is diffused through a porous plate and permitted to bubble up through the charge.

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[1] U. S. 2,314,615 (1943).

[2] GRUNDMANN, *Die Chem.*, **56**, 159 (1943).

When *n*-dodecane is nitrated at 180 to 190° by this procedure, the results presented in Table I are obtained.

TABLE I.—NITRATION OF DODECANE WITH HNO_3 VAPOR[1]
Per cent in reaction product

Ratio P:HNO_3	Dodecane	Nitrodecanes	Polynitrodecanes	Fatty acids
1:4	24	4	47	25
1:2	33	25	38	4
1:1	43	40	15	2
2:1	58	36	5	1

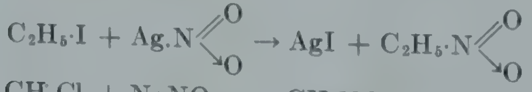
[1] Temp., 180 to 190°C.; density, HNO_3 = 1.40.

A similar diversity of reaction products was obtained by nitrating decane, hexadecane, and octadecane at 160 to 180°. The tabulated data show that a high ratio of nitric acid to paraffin results in the preponderant formation of polynitro compounds and fatty acids. When the acid ratio is reduced to 1:2, it is found that only 42 per cent of the paraffin has been used up and the principal products are mononitrododecanes. Some of the paraffin (up to 10 per cent depending on conditions) is destroyed through oxidative reactions.

In the nitration of paraffins with nitric acid, in both the liquid and vapor phase, the hydrocarbons having tertiary carbon atoms form nitro derivatives most readily. This is to be expected from the relative ease of nitration of aromatic compounds wherein all carbon atoms are necessarily tertiary. The secondary carbon atoms take on nitro groups with greater difficulty, and the primary compounds require the most drastic treatment.

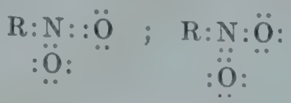
The nitroparaffins can also be made by the reaction of alkyl halides with certain metal nitrites and alkali metal nitrites.

$$C_2H_5{\cdot}I + AgO{\cdot}NO \rightarrow AgI + C_2H_5{\cdot}O{\cdot}N{\cdot}O \quad \text{Ethyl Nitrite} \qquad \text{IA}$$



$$C_2H_5{\cdot}I + Ag.N\!\begin{smallmatrix}\nearrow\!\!\!\!/\,O\\ \searrow O\end{smallmatrix} \rightarrow AgI + C_2H_5{\cdot}N\!\begin{smallmatrix}\nearrow\!\!\!\!/\,O\\ \searrow O\end{smallmatrix} \quad \text{Nitroethane*} \qquad \text{IB}$$

$$CH_3Cl + NaNO_2 \rightarrow CH_3NO_2 + NaCl\dagger \qquad \text{II}$$



$$R{:}\underset{\underset{:\ddot{\underset{\cdot\cdot}{O}}:}{\cdot\cdot}}{N}{::}\underset{\cdot\cdot}{\ddot{O}} \quad ; \quad R{:}\underset{\underset{:\ddot{\underset{\cdot\cdot}{O}}:}{\vdots}}{N}{:}\underset{\cdot\cdot}{\ddot{O}}{:}$$

The two isomers ethyl nitrite and nitroethane are always formed together

* The parachors for nitromethane, etc., show only one double bond, but dipole moment measurements indicate that the two oxygen atoms are in all probability equivalent because of a condition of resonance.

† U. S. 2,105,581 (1938).

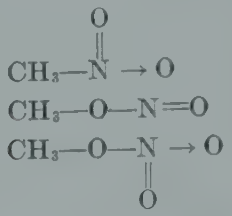
in reactions IA and IB. This is a characteristic phenomenon of such double decompositions and is ascribed to the fact that nitrous acid, as well as its noble metal salts, exists in isomeric forms. The alkali nitrites are strong electrolytes, whereas the colored noble metal nitrites do not dissociate. This difference arises because the former are probably derived from the true acid form and the latter from the neutral form of nitrous acid. The nitrous esters, having lower boiling points, may be separated from the nitro compounds by distillation.

TABLE II.—PHYSICAL PROPERTIES OF NITROPARAFFINS[1]

	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
Formula	CH_3NO_2	$CH_3CH_2NO_2$	$CH_3CH_2CH_2NO_2$	$CH_3CHNO_2CH_3$
Molecular weight	61.04	75.07	89.09	89.09
Sp. gr. at $\frac{20^\circ}{20^\circ}$ C.	1.139	1.052	1.003	0.992
Lb. U. S. gal. at 20°C.	9.48	8.75	8.35	8.24
Melting point, °C.	−29	−90	−108	−93
Boiling point, °C.	101.2	114.0	131.6	120.3
Flash point, °F. (Tag open cup)	112	106	120	103
Vapor pressure, mm. at 20°C.	27.8	15.6	7.5	12.9
Surface tension, dynes per cm. at 20°C.	37.0	31.3	30.0	30.0
Refractive index at 20°C.	1.3818	1.3916	1.4015	1.3941
pH 0.01M aqueous solution at 25°C.	6.4	6.0	6.0	6.2
Rate of evaporation, by weight (*n*-butyl acetate = 100)	180	145	100	124
Solubility at 20°C.:				
Ml. solvent in 100 ml. water	9.5	4.5	1.4	1.7
Ml. water in 100 ml. solvent	2.2	0.9	0.5	0.6

[1] USES: Solvents for cellulose acetate, cellulose triacetate, cellulose acetobutyrate, vinyl resins, nitrocellulose, synthetic resins, dyes, oils, fats, waxes, and many other organic materials. In the synthesis of organic compounds including dinitroparaffins, amines, diamines, alkylhydroxylamines, oximes, hydroxamic acids, carboxylic acids, aldehydes, ketones, halogenated nitro compounds, nitroalcohols, nitroglycols, nitroalkanetriols, organic esters of the three preceding types, inorganic esters (nitrates, phosphates), aminoalcohols, aminoglycols, aminoalkanetriols, aminoacetals, soaps of the four preceding types, nitroolefins, and nitroketones, which find use as rubber chemicals, emulsifying agents, pharmaceuticals, dyestuffs, photographic chemicals, insecticides, larvicides, wetting agents, textile chemicals.

The boiling points of nitromethane, methyl nitrite, and methyl nitrate are as follows:



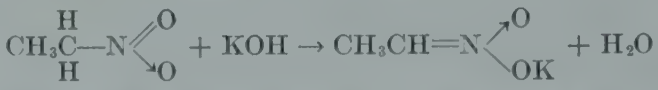
$CH_3-\overset{O}{\overset{\|}{N}}\rightarrow O$ 101°C.

$CH_3-O-N=O$ −12°C.

$CH_3-O-\underset{\underset{O}{\|}}{N}\rightarrow O$ 66°C.

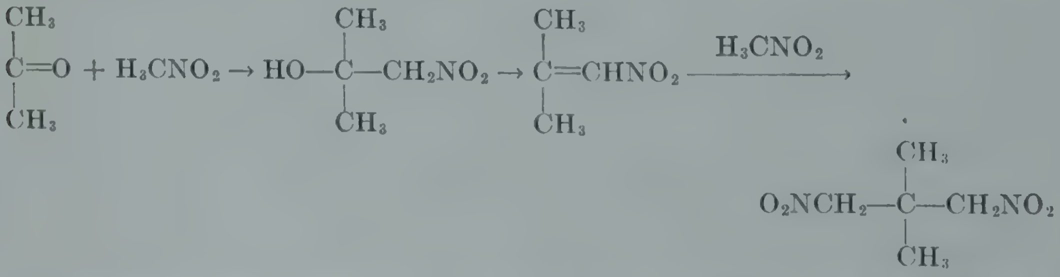
The nitroparaffins are colorless when pure and almost insoluble in water and have a characteristic mild chloroformlike odor. The physical properties of the simplest members are given in Table II on page 7.

Reactions of Nitroparaffins.—The nitroparaffins are quite reactive and can be employed as the raw materials for numerous syntheses having industrial importance.[1] The reaction of nitroparaffins with alkali and the displacement of an α-hydrogen atom by a metal are the reactions of the enol form. When nitroethane is treated with potassium hydroxide, the corresponding potassium derivative of the acinitro (nitronic acid) form, which is soluble in water, is obtained:



$$CH_3\overset{H}{\underset{H}{C}}-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + KOH \rightarrow CH_3CH=N\begin{smallmatrix}\nearrow O\\ \diagdown OK\end{smallmatrix} + H_2O$$

The nitroparaffins as well as the nitroalcohols can be reduced to primary amines by the use of iron and hydrochloric acid or hydrogen in the presence of a nickel catalyst. They can be condensed with ketones to form dinitroparaffins, the reaction between nitromethane and acetone presumably occurring as follows:



$$\underset{CH_3}{\overset{CH_3}{C}}=O + H_3CNO_2 \rightarrow HO-\underset{CH_3}{\overset{CH_3}{C}}-CH_2NO_2 \rightarrow \underset{CH_3}{\overset{CH_3}{C}}=CHNO_2 \xrightarrow{H_3CNO_2} O_2NCH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2NO_2$$

Primary or secondary nitroparaffins when treated with a base and a halogen simultaneously or in rapid succession give high yields of alpha halogen derivatives.

$$R_2CHNO_2 + NaOH \rightarrow R_2C=NO_2Na + H_2O$$
$$R_2C=NO_2Na + Cl_2 \rightarrow R_2CClNO_2 + NaCl$$

The nitroparaffins are characterized by reactions of the aldol type in which the hydrogen atoms attached to the carbon atom holding the nitro group may add to the oxygen of an aldehyde with the formation of hydroxyethyl-substituted nitroparaffins or nitroolefins, depending on conditions.

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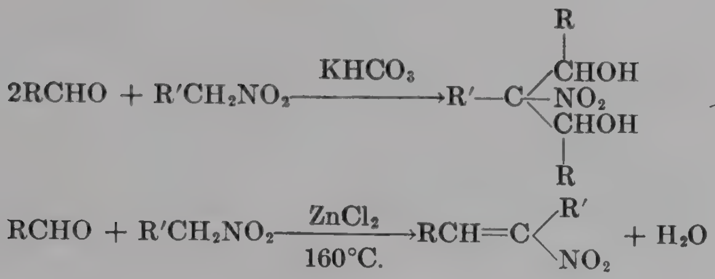
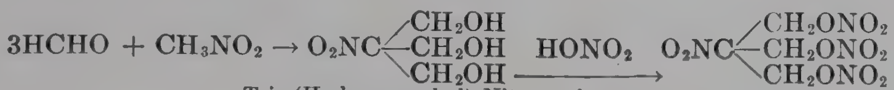
[1] HASS, *Ind. Eng. Chem.*, **35**, 1146 (1943).



$$2RCHO + R'CH_2NO_2 \xrightarrow{KHCO_3} R'{-}C\begin{array}{l} R \\ | \\ CHOH \\ NO_2 \\ CHOH \\ | \\ R \end{array}$$

$$RCHO + R'CH_2NO_2 \xrightarrow[160^\circ C.]{ZnCl_2} RCH{=}C\begin{array}{l} R' \\ NO_2 \end{array} + H_2O$$

As many molecules of the aldehyde unite with one molecule of nitroparaffin as there are α-hydrogen atoms, thus:



$$3HCHO + CH_3NO_2 \rightarrow O_2NC\begin{array}{l} CH_2OH \\ CH_2OH \\ CH_2OH \end{array} \xrightarrow{HONO_2} O_2NC\begin{array}{l} CH_2ONO_2 \\ CH_2ONO_2 \\ CH_2ONO_2 \end{array}$$

Tris (Hydroxymethyl) Nitromethane or
2-Hydroxymethyl-2-nitro-1, 3-propanediol

The nitroalcohols on further esterification with nitrating acids yield nitrates having the structure and properties similar to the well-known glyceryl trinitrate.

Nitric Acid Esters of Aliphatic Compounds.—The nitration of aliphatic polyhydroxy alcohols and of carbohydrates results in the formation of nitric acid esters. These compounds, although popularly referred to as nitro compounds, are true nitrates:

$K{-}O{-}NO_2$;	$C_3H_5(O{-}NO_2)_3$;	$C_{24}H_{30}O_{10}(O{-}NO_2)_{10}$
Potassium Nitrate	Glyceryl Trinitrate	Cellulose Decanitrate

The nitrates of glycerol, glycol, cellulose, starch, and sugar are probably the most important members of this group of esters and are discussed in greater detail under Esterification. Although these compounds are used as military explosives, their principal uses are in normal and highly important industrial undertakings. The employment of cellulose esters in the manufacture of synthetic ivory, lacquers, Cellophane, artificial leathers, etc., is well known. The mining of coal, copper, and other minerals; the blasting of rocks and stumps; the excavating and irrigating operations are only a few of the normal activities that require several hundred millions of pounds of explosives annually.

The nitrating agent generally employed in the preparation of these esters is a mixed acid comprising nitric and sulfuric acids in varying proportions. In the nitration of glycerol, both the total acidity and nitric acid concentration of the mixed acid are greater than those employed for the nitration of carbohydrates. Typical analyses would show the following compositions:

Compound nitrated	Composition of nitrating acid, %			
	H_2SO_4	HNO_3	HNO_2	H_2O
Glycerol	55	44.8	0.2	0
Cellulose	74	18.0	0.6	7.4

In the United States, mixed acids containing free SO_3, *i.e.*, having an acidity of over 100 per cent, are generally used for the manufacture of glyceryl trinitrate.

Aromatic Nitro Compounds.—Practically all the nitrating agents previously enumerated (page 1) are used in the preparation of nitroaromatic compounds. Economic considerations are generally the determinants in the choice of the agent. Often, however, certain inherent chemical or physical properties or the presence of substituents necessitate the use of specific nitrating agents. The choice of the nitrating agent may furthermore determine the position of the entering nitro group. The important subject of orientation therefore merits a brief consideration at this time.

Orientation of Nitro Groups in Aromatic Compounds.—*In the benzene series*, three different dinitrobenzenes can be obtained—the ortho, meta, and para compounds. The position taken by the entering nitro group depends on the group already present. As a rule, it enters in a position *meta* to a nitro, sulfonic acid, carboxyl, or carbonyl group and *ortho* and *para* to a chloro, bromo, alkyl, amino, or hydroxyl group. The proportions in which the isomerides are formed depend to a slight extent on

TABLE III.—THE NITRATION OF VARIOUS MONOSUBSTITUTED BENZENES[1]

Group already present	Percentage of		
	Ortho	Meta	Para
F	12.4	Trace	87.6
Cl	30.1	Trace	69.9
Br	37.6	Trace	62.4
I	41.1	Trace	58.7
CH_3	58.8	4.4	36.8
CH_2Cl	40.9	4.2	54.9
$CHCl_2$	23.3	38.8	42.9
CCl_3	6.8	64.5	28.7
$COOC_2H_5$	28.3	68.4	3.3
COOH	18.5	80.2	1.3
NO_2	6.4	93.2	0.25

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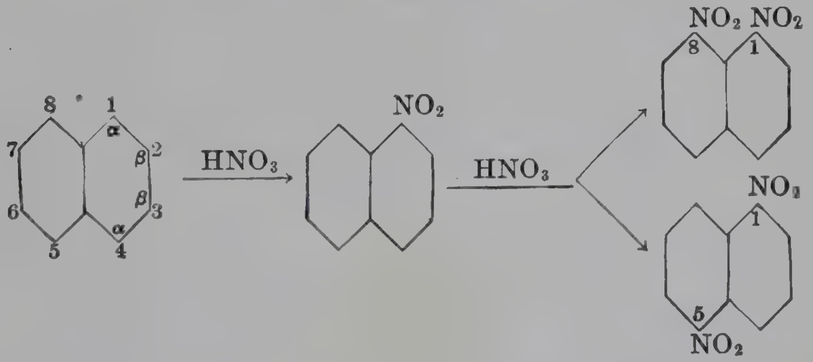
[1] HOLLEMAN, *Chem. Rev.*, **1,** 187 (1925).

the nitrating temperature. A lower temperature of nitration is conducive to the exclusive formation of the meta derivatives in the first group and a preponderance of para compound in the second. In case two or more groups are already present, it is difficult to predict which compound will be formed owing to the conflicting influences of these groups, and often a mixture of different compounds will result upon nitration. In most cases, however, it is possible to regulate the conditions to be optimal for a certain compound and thus minimize the formation of undesirable by-products. Upon purification, it is generally possible to obtain a product suitable for technical operations.

The influence of substituents in the benzene ring upon the orientation of the entering —NO_2 group is shown in Table III.

Naphthalene Series.—In the naphthalene series, it is possible to have two different mononitro derivatives, *viz.*, the alpha and beta compounds, but the beta compound is formed only to a slight extent by direct nitration. Upon nitration, the first nitro group enters almost exclusively into the alpha position; a second nitro group enters into position 5 or 8.



Anthraquinone Series.—In the anthraquinone series, nitration with mixed acids containing a slight excess over one equivalent of nitric acid results in the formation of three nitro derivatives. These are the alpha-substituted 1-nitroanthraquinone and the 1, 5- and 1, 8-dinitroanthraquinones. Unless the nitric acid ratio and concentration are sufficient to ensure considerable dinitration, some anthraquinone remains unreacted.

Nitration of Amines and Phenols. Acylation.—Since amino compounds are very susceptible to oxidation, it is generally necessary to protect the —NH_2 group during nitration. This is accomplished by converting the amine to its acyl derivative. Acylation may be carried out by heating the amine under a vented reflux with acids or acid chlorides.

$$R{\cdot}NH_2 + R{\cdot}COOH \rightarrow R{\cdot}NH{\cdot}CO{\cdot}R + H_2O \tag{I}$$
$$R{\cdot}NH_2 + R{\cdot}CO{\cdot}Cl \rightarrow R{\cdot}NH{\cdot}CO{\cdot}R + HCl \tag{II}$$

Acetic acid and, to a lesser extent, oxalic and formic acids are employed for acylations according to Eq. (I); acetyl chloride, benzoyl chloride, and *p*-toluenesulfonyl chloride are suitable for reactions according to Eq. (II).

The choice of acylating agent and nitrating agent is often a matter of importance, since the orientation of the entering —NO_2 group is, as can

TABLE IV.—NITRATION OF ANILINE AND ANILIDES[1]

A. Nitration with 80 Per cent HNO_3 in Glacial Acetic Acid

Amine	Per cent			Ratio ortho:para
	Para	Ortho	Meta	
Free amine	64	38	..	1:1.8
Acetyl	70	30	..	1:2.3
Benzoyl	72	28	..	1:2.6
Formyl	74	26	..	1:2.8
Chloroacetyl	75	25	..	1:3.0
Amino oxalyl	79	21	..	1:3.8
Toluenesulfonyl	84	16	..	1:5.3

B. Nitration with 94 Per Cent HNO_3 in Concentrated H_2SO_4

Amine	Per cent			Ratio ortho:para
	Para	Ortho	Meta	
Free amine	50	1	49	
Acetyl	92	8	..	1:11.5
Benzoyl	93	7	..	1:13.3
Formyl	94	6	..	1:15.6
Chloroacetyl	96	4	..	1:24.0
Amino oxalyl	98	2	..	1:49.0
Toluenesulfonyl	98	2	..	1:49.0

C. Nitration in HNO_3

Amine	Per cent			Ratio ortho:para
	Para	Ortho	Meta	
Aniline nitrate	56	4	40	
Acetyl	58	42	..	1:1.4
Benzoyl	60	40	..	1:1.5
Formyl	65	35	..	1:1.9
Chloroacetyl	73	27	..	1:2.7
Oxalyl	85	15	..	1:5.7
Toluenesulfonyl	88	12	..	1:7.3

Temperature, 20°C.; time, 24 hr.

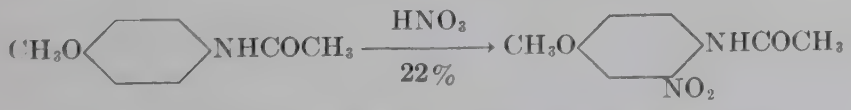
[1] According to LAUER, *J. prakt. Chem.*, **137**, 175 (1933).

be seen from Table IV, affected by the agents employed. When acetanilide is nitrated with a mixed acid in the presence of an excess of sulfuric acid (see pages 54, 55) at 3 to 5°C., the product is principally *p*-nitroacetanilide, only a small quantity—2 to 5 per cent of the ortho isomer—being formed. When the nitration of acetanilide is carried out with a mixed acid comprising glacial acetic acid and fuming nitric acid at 0 to 5° in the presence of a small quantity of urea, the ratio of ortho to para isomerides is 3:1. When nitration is accomplished by acetyl nitrate in acetic anhydride, the ortho compound is obtained almost exclusively.

The nitration of *p*-toluenesulfonyl derivatives of amines is effected with (1) nitric acid alone; (2) a mixture comprising nitric and acetic acids; or (3) boiling glacial acetic acid containing sodium nitrite. Nitration with mixed acids, *i.e.*, $HNO_3—H_2SO_4$ mixtures, may result in nitration in the toluene nucleus also. Thus, Reverdin found that the *p*-toluene-sulfonyl derivative of *p*-anisidine gave 3-nitro-*p*-anisidine on nitration with nitric acid (sp. gr., 1.4) in acetic acid at 10 to 22°C., whereas a nitro group was also introduced into the toluene nucleus when nitration was effected with mixed acid at subzero temperatures.[1]

It is interesting to note that in exceptional cases, where it is possible to nitrate amino compounds without resorting to previous acylation, the product differs from that obtained by the nitration of the acyl derivative. When *p*-toluidine is dissolved in a large quantity of sulfuric acid and nitrated with mixed acid ($HNO_3—H_2SO_4$ mixture) at low temperatures, 2-nitro-*p*-toluidine is obtained. The nitration of the acetyl derivative yields 3-nitro-*p*-toluidine.

Phenols, like amines, are particularly susceptible to oxidation; and, in some nitrations, it is therefore advisable to acylate first, *i.e.*, to form an ester and to use mild conditions. The nitrated derivative, on hydrolysis, yields the nitrophenol. When an aromatic amine contains also an ether group, particularly mild nitrating conditions must be used. Thus, 4-acetylamino-anisole can be converted to 3-nitro-4-acetylamino-anisole with a yield of 80 per cent by nitrating with a dilute, 22 per cent nitric acid.[2]



II. NITRIC ACID IN THE NITRATION PROCESS

Assuming that nitric acid reacts according to the following equation:

$$R{\cdot}H + HO{\cdot}NO_2 \rightarrow R{\cdot}NO_2 + H_2O$$

[1] Reverdin, *Bull. soc. chim. ind.*, **35**, 1168 (1924).

[2] U. S. 2,325,797 (1943).

it can be seen that the aqueous solution containing the active nitrating agent becomes more and more dilute as nitration progresses. For example, when 2 moles of 90 per cent aqueous HNO_3 are used to effect the nitration, the HNO_3 concentration of the residual acid, after 1 mole of the mononitro compound is formed, will be

$$\frac{63}{140 - 63 + 18} = 66.3\%\ HNO_3$$

If 3 moles of 70 per cent aqueous HNO_3 are employed, the HNO_3 concentration after mononitration will be

$$\frac{126}{270 - 63 + 18} = 56\%\ HNO_3$$

With diminishing HNO_3 concentration, two important problems are introduced: (1) The nitrating capacity of the acid is greatly reduced; and (2) its activity as an oxidizing agent is relatively increased. Obviously, also, the factor of cost is involved in the employment of such large excesses of nitric acid.

The dual activity of nitric acid may be explained as follows:[1] Spectroscope investigations show that alkali salts and esters of nitric acid show quite different absorption spectra in the ultraviolet and must therefore be differently constituted. The concentrated acid shows a spectrum that is identical with that of esters, whereas that of the dilute acid that undergoes dissociation is the same as that of the alkali salts.[2] Acids of medium concentration can give both spectra together.

In studying the equilibrium of aqueous nitric acid solutions, Hantzsch found that liquid nitric acid is dimolecularly associated.[3] The relationship between the pseudoacid (neutral form) $HO{\cdot}NO_2$ and the true acid $H{\cdot}NO_3$ for acids of varying concentrations was found by him to be as follows:

HNO_3, %	Normality	Moles H_2O per mole HNO_3	Pseudoacid, %[1]	Undissociated true acid, %	Ionized true acid NO_3^- H^+, %
77.3	18	1.0	70	25	5
48.3	10	3.75	50	32	18
31.6	6	7.5	2	60	38

[1] Hantzsch further indicated that strong nitric acid is a mixture of pseudoacid $(NO_2)(OH)$, nitronium nitrate $((HNO)_3N)(NO_3)_2$, and hydroxonium nitrate $(NO_3)(H{\cdot}OH_2)$, or $(NO_3)'(OH_3)^+$.

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[1] EPHRAIM, "Inorganic Chemistry," p. 583, 1926 ed.

[2] Radiation with respect to Raman effect also indicates the molecular form $NO_2{\cdot}OH$ exists in concentrated nitric acid. BRUNETTI and OLLANO, *Atti accad. Lincei*, **13**, 52 (1931).

[3] HANTZSCH, *Ber.*, **54**, 954 (1925).

It was also determined that the percentage of pseudoacid increases with temperature and that nitric acid vapor is made up entirely of NO_2OH and is therefore a more effective nitrating agent than the liquid acid. This has been found to be true for the nitration of the higher paraffins and aromatic hydrocarbons.[1]

Othmer and coworkers have found a practical way of overcoming the unfavorable factors inherent in the use of nitric acid as a nitrating agent.[2] It was ascertained that the water of nitration could be removed with benzene as a binary azeotropic mixture from the system benzene, 60 to 66 per cent nitric acid and water. These findings suggested the possibility of removing the water of nitration in a continuous manner, thus maintaining a constant and practical nitric acid concentration in the nitrating system. Other pertinent evidence showed that with increasing acid concentration the distribution of nitric acid in benzene increases in accordance with the following data:

% HNO_3 in water layer	% HNO_3 in benzene layer	% HNO_3 in water layer	% HNO_3 in benzene layer
6.3	0.0	47.5	2.9
7.6	0.0	49.0	3.0
40.0	2.6	58.0	4.16
43.5	2.7	61.3	4.45

These investigators also determined the relationship between nitric acid concentration and rate of formation of nitrobenzene (Fig. 2). Since the concentration of nitric acid in the aqueous layer is related to its distribution in the benzene phase, these curves indicate (1) that at least 2 per cent nitric acid is needed in the benzene phase and (2) that agitation—which can be provided by using HNO_3 vapors—increases the velocity of reaction. Other experimental evidence confirmed previous knowledge that the degree and rate of nitration are functions of the nitric acid concentration. The curves of Fig. 3, *A* and *B*, and supporting data indicate clearly that when the HNO_3 concentration falls below 50 per cent in nonagitated systems and below 40 per cent in agitated mixtures, nitration practically ceases.

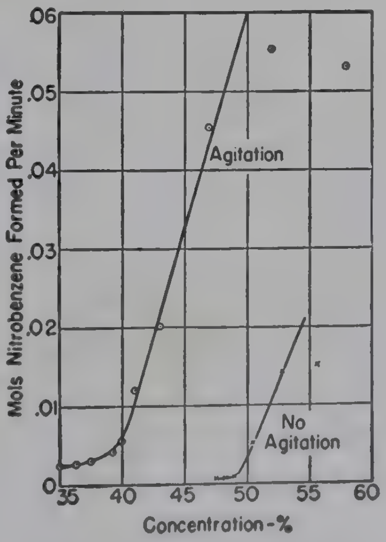

Fig. 2.—Rate of formation of nitrobenzene *vs.* concentration of nitrating acid in water layer.

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[1] Grundmann, *Die Chem.*, **56**, 159 (1943).

[2] Othmer, Jacobs, and Levy, *Ind. Eng. Chem.*, **34**, 286 (1942); **36**, 447 (1944).

Based on the preceding findings and observations, a method has been suggested by Othmer for the continuous nitration of benzene with nitric acid of 61 per cent concentration, wherein the water of nitration is removed as a binary azeotrope from which benzene is separated and returned to the nitration as a reflux, thus preventing the escape and loss of nitric acid (see technical section). The nitration of toluene, which also has the capacity to entrain water, can be carried out in a similar manner.[1]

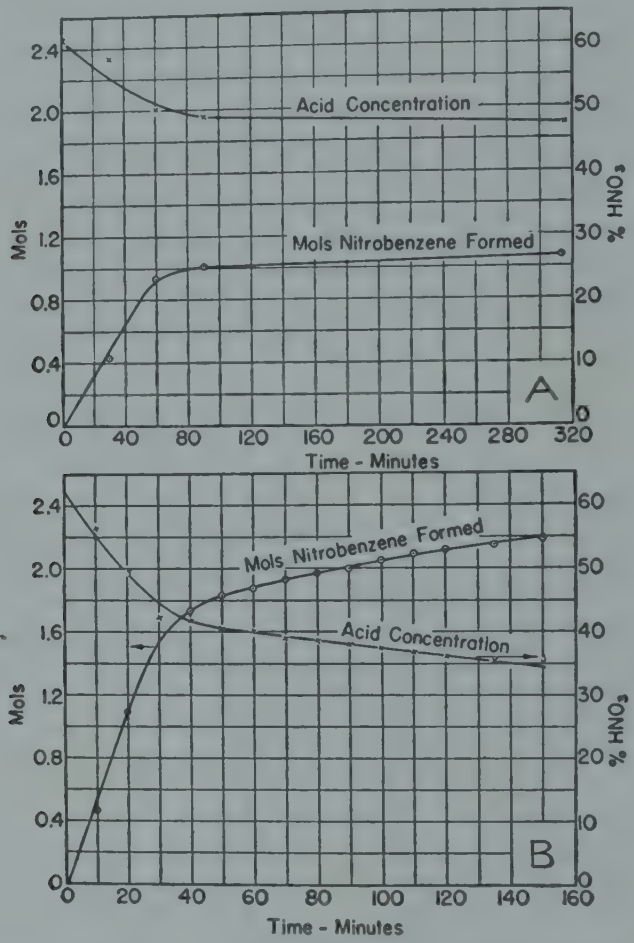

FIG. 3.—Conversion of benzene and nitric acid to nitrobenezene.

A. Batch run without agitation.
B. Batch run with agitation.

III. MECHANISM OF THE NITRATION REACTION

Aromatic Compounds.—According to Michael, the first phase of nitration is an aldolization.[2] Acceptance of this viewpoint not only accounts for the nitration of aromatic compounds but also elucidates the mechanism through which the nitro group actually becomes attached to the carbon. Accordingly, in the nitration of aromatic compounds, a reactive nuclear hydrogen unites with a Δ-oxygen, *i.e.*, =O, of the acid, and the residual aromatic group with the nitrogen, the elements of water then separating from the addition product. The nitration of benzene with nitric acid and nitrosulfuric acid may be set forth as follows:

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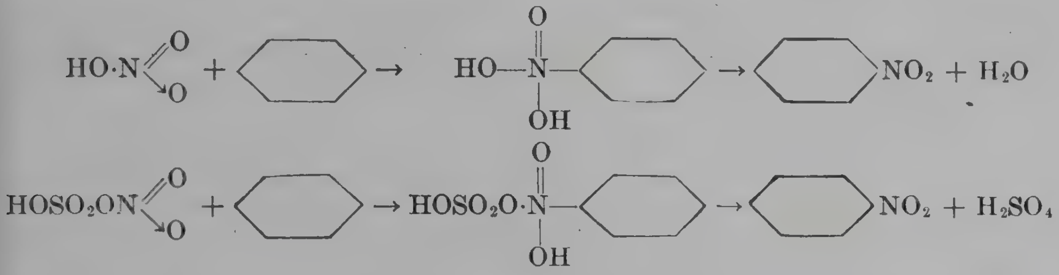
[1] OTHMER and KLEINHANS, JR., *Ind. Eng. Chem.*, **36**, 447 (1944).

[2] MICHAEL, *Ber.*, **29**, 1795 (1896); MICHAEL and CARLSON, *J. Am. Chem. Soc.*, **57**, 1269 (1935).



The course of nitration through aldolization is coordinated with one of the largest classes of organic reactions. These are nucleus syntheses, *i.e.*, condensations, and are based on the fundamental organic principle that substitution reactions involving a delta group always proceed through addition at the delta atoms followed by elimination; *i.e.*, they are pseudo substitutions.[1] In the nitration process, the dominating forces in nitric acid and its anhydrides are the chemical potential and chemical affinity of a Δ-oxygen for a reactive nuclear H and that of N for aryl as indicated graphically above.

Olefins.—Nitrogen tri- and tetroxides, which may be considered as simple and mixed anhydrides of nitrous and nitric acids, show a highly developed additive capacity to ethylene derivatives forming nitro and nitroso derivatives instantaneously. Correspondingly, nitrosulfuric acid should form nitrosulfuric ester addition products with ethylene,[2] the

$$CH_2{:}CH_2 + HOSO_2O{\cdot}NO_2 \rightarrow CH_2OSO_2OH{\cdot}CH_2NO_2$$

sulfuric ester group being subsequently displaced by the stronger nitric ester radical forming the nitro nitric ester and pyrosulfuric acid as follows:

$$CH_2OSO_2OHCH_2NO_2 + HOSO_2ONO_2 \rightarrow CH_2(ONO_2)CH_2NO_2 + H_2S_2O_7$$

Michael and Carlson[3] have shown quite conclusively that the formation of the nitric acid ester of ethylene nitrohydrin with a mixture of fuming sulfuric and nitric acids does not proceed as Wieland[4] had postulated, *viz.*, by addition of HO and NO_2 to ethylene and subsequent action of nitric acid. The acid mixture must contain the mixed anhydride nitrosulfuric acid, which reacts as indicated above.[1]

When concentrated nitric acid is employed in the nitration of alkyl-

[1] Michael, *Ber.*, **29**, 1795 (1896); Michael and Carlson, *J. Am. Chem. Soc.*, **57**, 2169 (1935).

[2] Michael and Carlson, *J. Am. Chem. Soc.*, **57**, 1269 (1935).

[3] *Ibid.*

[4] Weiland and coworkers, *Ber.*, **53**, 201 (1920); **54**, 1770 (1921).

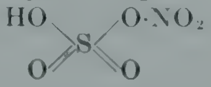
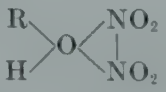
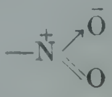
enes, the nitroalkane nitric esters obtained are *not* direct products of nitration but are due to the union of ethylene with nitric oxides formed in the deoxidation of nitric acid. Oxidation is always apparent in such indirect nitrations.

Paraffins.—The nitration of paraffins with nitric acid in the liquid phase is known to be accompanied by oxidative reactions leading to the formation of higher oxides of nitrogen. The mechanism of nitration is, however, quite obscure.

IV. EXAMINATION OF NITRATING AGENTS

It is of interest, in the light of the previous discussion, to examine the more important of the nitrating agents which are tabulated below.

EXAMINATION OF NITRATING AGENTS

Nitrating agents	Remarks	Structural formulation	Acid liberated
Nitric acid[1].........	Pseudoacid	$(HO \cdot NO_2)_2$	$(H \cdot OH_2)^+$, $(NO_3)^-$
Nitric acid anhydride[2]	N_2O_5	$O_2N \cdot O \cdot NO_2$	HNO_3
Nitrosulfuric acid....	Mixed acid anhydride		H_2SO_4
Acetyl nitrate.......	Mixed acid anhydride	$CH_3CO \cdot O \cdot NO_2$	CH_3COOH
Benzoyl nitrate......	Mixed acid anhydride	$C_6H_5CO \cdot O \cdot NO_2$	C_6H_5COOH
Diacetyl-*o*-nitric acid[1]	From nitrates and glacial acetic acid	$(CH_3 \cdot COOH)_2HO \cdot NO_2$	CH_3COOH
Nitrogen tetroxide...	Mixed acid anhydride, probably yielding indicated addition complex		HNO_2
Nitrogen dioxide....	Photochemical excitation		HNO_2

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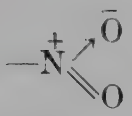
[1] Hantzsch has shown that concentrated nitric acid is dimolecular and exists principally in the pseudoacid form. The reaction with the formation of hydroxonium nitrate represents the viewpoint of Hetherington and Masson.

[2] When alkali nitrates and sulfuric acid are used, the HNO_3 liberated in the presence of the dehydrating agents H_2SO_4—$NaHSO_4$ presumably reacts as N_2O_5. The qualitative study of mixtures of H_2SO_4, HNO_3 and H_2O by the Raman effect has shown that, in mixtures which contain little water, nitric acid is totally or partially dehydrated into its anhydride, N_2O_5.

It is apparent from an examination of the formulations for the nitrating agents that the following generalizations can be made. The nitrating agents are complexes that:

1. Contain the  group as part of a labile complex.

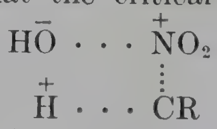
2. Are similar in structure to nitric acid esters, or acid anhydrides, and generally have the $—NO_2$ group held by a shared oxygen atom.

3. Possess pronounced auxiliary valence, *i.e.*, accept electrons at and share electrons at $—\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}—$ atoms.

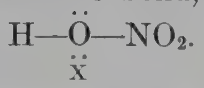
4. On stabilization after nitration, split off an acid.

5. Under certain circumstances, *e.g.*, nitration of amines, the acid split off may participate in a second reaction. *o*-Nitroacetanilide is thus made directly from aniline by reacting with acetyl nitrate or diacetyl-*o*-nitric acid. The fission in the nitrating complex occurs in the $—O|\cdot NO_2$ group.

When nitric acid is the active agent, it appears that the critical complex with hydrocarbons can be represented thus:



$$\begin{array}{ccc} H\bar{O} & \cdots & \overset{+}{N}O_2 \\ & & \vdots \\ \overset{+}{H} & \cdots & \dot{C}R \end{array}$$

Any coreactant that could facilitate the fission of the $\bar{O}—\overset{+}{N}$ bond would obviously aid the reaction. This evidently can be accomplished by the introduction of a strong acceptor such as sulfuric acid or sulfur trioxide which, by forming a coordinate bond, would cause a shift of electrons toward the oxygen atom,  $H—\underset{\underset{X}{\cdot\cdot}}{\overset{\cdot\cdot}{O}}—NO_2$.

Mixed Acids for Nitrations.—It has been shown that nitric acid alone is generally a poor nitrating agent, since its constitution undergoes change during the nitration process because water is introduced. To overcome this difficulty, it is necessary to provide means for the continuous removal of the water of nitration (see pages 46, 47), in order to maintain a relatively constant and satisfactory HNO_3 concentration, or to employ a very large excess of nitric acid. Under the latter circumstances, polynitro derivatives may be formed by the substitution of nitro groups for two or more hydrogen atoms. In the presence of dehydrating acids, most mononitrations can be carried out with approximately the theoretical amount of nitric acid, because nitration is presumably carried out with the mixed anhydride $HOSO_2\cdot O\cdot NO_2$

$$HONO_2 + H_2SO_4 \rightarrow \underset{\text{Nitrosulfuric Acid}}{HOSO_2O\cdot NO_2} + H_2O$$

$$HOSO_2\cdot ONO_2 + R\cdot H \rightarrow R\cdot NO_2 + H_2SO_4$$

As nitration progresses, sulfuric acid is split off and forms hydrates, and its capacity for further dehydration diminishes.

Notwithstanding the widespread belief that nitrosulfuric acid is the active nitrating agent, there is evidence that N_2O_5 is also formed as a result of the dehydrating action of concentrated sulfuric acid. From a study of mixed acids of 100 per cent total acidity by the Raman effect. Chedin obtained the following data:[1]

HNO_3	10	20	40	60	80
H_2SO_4	90	80	60	40	20
N_2O_5	10	12.5	11.5	10	7.8
$HONO_2$	0	7.5	28.5	50	72.2

When water is present in the mixed acid, the percentage of nitric acid anhydride is markedly diminished. Thus a mixed acid comprising 80, 10 and 10 per cent H_2SO_4, HNO_3 and H_2O, respectively, contains only 3.4 per cent N_2O_5. Inasmuch as the water content of the nitrating acid increases during the progress of the reaction and because the nitric acid content of the mixed acid is practically exhausted in effecting mononitrations, it is necessary to assume that nitric acid is present also in another active form throughout the liquid-phase nitration process. By combining with sulfuric acid, it forms a compound with greater chemical energy. The similar preparation and successful employment of other analogous mixed anhydrides, *e.g.*, benzoyl nitrate and acetyl nitrate, constitute further evidence that nitrosulfuric acid ($HOSO_2O{\cdot}NO_2$) is the reactive component in mixed acid.

It is important to observe that the employment of mixed acids rather than an excess of nitric acid results in certain technical advantages. Since nitric acid is much more expensive than sulfuric acid, a considerable saving is effected. The sulfuric acid, moreover, is recovered from the spent acid with only a slight loss. In addition to serving as an economical dehydrating agent, the presence of sulfuric acid (as will be shown later) makes it easier to keep the reaction under control, and the milder conditions that are thus provided are instrumental in inhibiting the formation of oxidation products. The greatest advantage, however, relates to the *industrial* use of mixed acid; for unlike nitric acid, it corrodes the storage equipment and nitrating apparatus only to a very slight extent. The low hydrogen-ion concentration of mixed, or spent, nitrating acids having a total acidity in excess of 78 per cent explains why they do not appreciably attack steel at ordinary nitrating temperatures. This fact is of great engineering importance, as it makes possible the use of iron apparatus in nitration operations.

Nitrations with Alkali Nitrates and Sulfuric Acid.—The nitric acid in mixed acids may be prepared *in situ* by using alkali nitrates and sulfuric acid. When this method is employed, it is necessary to use somewhat more sulfuric acid, since the reaction

$$NaNO_3 + NaHSO_4 \rightarrow HNO_3 + Na_2SO_4$$

---

[1] CHEDIN, *Compt. rend.*, **202**, 1067 (1936).

takes place best at temperatures so high that the equilibrium

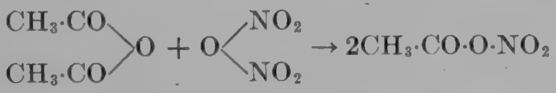
$$2HNO_3 \rightleftarrows N_2O_5 + H_2O$$

is affected. The increased velocity of decomposition of N_2O_5 results in the formation of NO_2 and, O; and, in the reestablishment of the preceding equilibrium, more water is introduced. Therefore, any method that diminishes the temperature at which HNO_3 is liberated is favorable. For this reason, the cheaper $NaNO_3$, which decomposes at a lower temperature than does KNO_3, is used. The nitric acid liberated in this way is practically free of water.

It is interesting to recall that in the infancy of the dye industry Perkin employed this method of nitration because no other satisfactory method was then available for obtaining nitrating acids of high total acidity.

A number of patents have been taken out utilizing this procedure, particularly for the preparation of nitrochlorobenzenes. This method of nitration is unquestionably of great value in plants not possessing facilities for the denitration and concentration of spent acids. Generally speaking, however, the substitution of nitrates introduces mechanical difficulties as well as problems in obtaining a pure product and consequently has been adopted to only a limited extent.

Nitrations with Organic Nitrates.—Pictet found that acetic anhydride and nitric acid anhydride N_2O_5 combine to form acetyl nitrate:[1]



$$\left.\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\right>O + O\left<\begin{matrix}NO_2\\ NO_2\end{matrix}\right. \rightarrow 2CH_3\cdot CO\cdot O\cdot NO_2$$

An analogous nitrate was prepared by Francis through a double decomposition involving benzoyl chloride and silver nitrate:[2]

$$C_6H_5\cdot CO\cdot Cl + AgO\cdot NO_2 \rightarrow AgCl + C_6H_5\cdot CO\cdot O\cdot NO_2$$

Both acetyl and benzoyl nitrates are energetic nitrating agents for aromatic compounds dissolved in carbon tetrachloride or acetic anhydride.[3] These nitrates react readily with alcohols, yielding nitric acid esters. Acetyl nitrate as well as diacetyl nitrate can nitrate and acetylate amines. When 1 mole of acetyl nitrate reacts with 2 moles of aniline dissolved in carbon tetrachloride at $-15°C.$, equimolecular proportions of acetanilide and aniline nitrate are obtained. On further nitration with a larger ratio of acetyl nitrate, *o*-nitroacetanilide is obtained.

In carbon tetrachloride, both acetyl nitrate and benzoyl nitrate convert acetanilide principally to *o*-nitroacetanilide ($o = 84.9$ per cent; $m = 0.2$ per cent; $p = 14.9$ per cent).

---

[1] PICTET, *Ber.*, **40**, 1163 (1907).

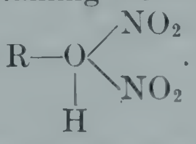
[2] FRANCIS, *Ber.*, **39**, 3798 (1906).

[3] These agents may react with explosive violence.

Nitrations with Metal Nitrates.—Numerous metal nitrates, particularly those which have a low decomposition temperature, can, in acetic anhydride, or glacial acetic acid solution, serve as nitrating agents.[1] Cupric, ferric, and aluminum nitrates are satisfactory substitutes for nitric acid in this process. The procedure is characterized by the dual activity of the acetyl nitrate mixture. When amines are reacted upon, both acetylation and nitration occur. Thus, *o*-nitroacetanilide is obtained by treating aniline in acetic anhydride with cupric nitrate at 30°C.

When phenol in acetic anhydride is reacted upon by ferric nitrate dissolved in acetic anhydride, picric acid is obtained directly. Benzene, chlorobenzene, etc., can similarly be converted to mononitro compounds.

Nitration with Nitrogen Peroxide.[2]—Whereas nitric acid anhydride is one of the most vigorous of nitrating agents, nitrogen tetroxide alone exhibits very little reactivity with benzene, chlorobenzene, or toluene. When such reactions are allowed to proceed for weeks, only small quantities of oxidation and reduction products are formed. This behavior is to be attributed to the weak capacity of N_2O_4 to add to benzenoid compounds not containing the —OH group which would permit the formation of the complex



$R{-}\underset{\displaystyle H}{\overset{}{O}}\!\begin{smallmatrix}\diagup NO_2\\ \diagdown NO_2\end{smallmatrix}$.

Although nitrogen tetroxide adds immediately to olefins, the reaction is very complex, since mixtures of easily decomposed substances are obtained.

With increasing substitution in the benzene ring, the capacity of the aromatic compound to react with N_2O_4 alone increases. Naphthalene is readily nitrated by means of nitrogen tetroxide. The initially formed N_2O_4 addition compound decomposes soon after its formation into nitrous acid and nitronaphthalene. Aniline and phenol react with N_2O_4 with similar ease, catalysts being unnecessary in the treatment of these compounds. If $AlCl_3$ be added, N_2O_4 exerts a violent oxidizing effect. It is interesting to note that naphthalene reacts smoothly with N_2O_4 in carbon tetrachloride solution but is indifferent in ether solution. This difference is due to the formation of an addition compound of N_2O_4 with ether, which no longer is capable of addition to naphthalene.

Silica gel, like $AlCl_3$, apparently has the power to activate a hydrogen atom in the benzene ring; and at 310°C., it can be used as a specific catalyst for the vapor-phase nitration of benzene with nitrogen dioxide (NO_2). McKee and Wilhelm found that the percentage nitration was a function of the ratio $NO_2{:}C_6H_6$.[3] When the mole fraction of NO_2 in the binary reaction mixture is 0.88, the conversion of benzene to nitrobenzene is approximately 83 per cent. Accompanying the nitration reaction, there is a reduction of approximately 1.5 moles of nitrogen dioxide to nitric oxide per mole of nitrobenzene produced. In operations involving the recycling of exit gases, the nitric oxide would, of course, have to be reoxidized.

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[1] MENKE, *Rec. trav. chim.*, **44**, 141, 270 (1925).

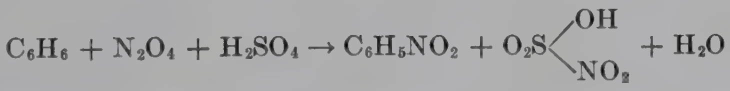
[2] At low temperatures, nitrogen peroxide has a molecular weight corresponding to N_2O_4; on vaporization it is practically completely dissociated to the dioxide.

[3] McKEE and WILHELM, *Ind. Eng Chem.*, **28**, 662 (1936).

$$\underset{\text{Colorless}}{2NO + O_2} \rightleftharpoons \underset{\text{Brown}}{2NO_2} \rightleftharpoons \underset{\text{Colorless}}{N_2O_4}$$

When phenols are dissolved in a benzene solution of nitrogen tetroxide, they are readily nitrated. In this way, *o*- and *p*-nitrophenols are obtained from phenol. Similarly, *o*-cresol yields 3- and 5-nitro-*o*-cresols, and cellulose yields cellulose nitrates.[1]

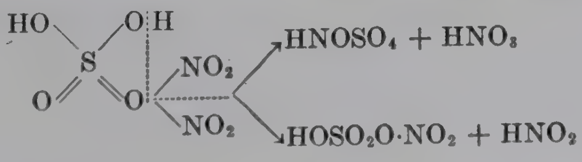
Nitrogen tetroxide in the presence of strong sulfuric acid[2] is a good nitrating agent, and yields of approximately 90 per cent of the theoretical have been obtained with it in the nitration of benzene, toluene, and naphthalene. Pinck states that "in such a system, about 50 per cent of the nitrogen tetroxide is utilized in the nitration of the organic substance, and approximately 50 per cent is combined with the sulfuric acid in the form of nitrosylsulfuric acid."[2] The complete reaction for a single-step nitration for benzene, for example, can be represented by the following equation:



$$C_6H_6 + N_2O_4 + H_2SO_4 \rightarrow C_6H_5NO_2 + O_2S\begin{cases}OH\\NO_2\end{cases} + H_2O$$

The intermediate steps of the nitration process are as yet obscure. The addition complex of nitrogen tetroxide with sulfuric acid (*A*), which would contain the —O—NO_2 group, may well be the active agent. The formation of similar oxonium compounds presumably accounts for the successful nitration of phenols and carbohydrates with N_2O_4.

(*A*)



(*B*)

(*C*)

There is also the possibility that the moderately active nitric acid may be liberated along with nitrosylsulfuric acid (*B*). Most probably the addition complex liberates the mixed anhydride nitrosulfuric acid ($HOSO_2O{\cdot}NO_2$) and HNO_2. The HNO_2 will here combine with the excess of H_2SO_4 to produce the end product found by Taylor[3] and by Pinck,[2] *viz.*, $HNOSO_4$.

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[1] U. S. 1,917,400 (1933).

[2] Pinck, *J. Am. Chem. Soc.*, **49**, 2536 (1927).

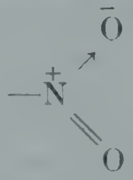
[3] Taylor and Richardson, U. S. 1,640,737 (1927).

Catalytic NO_2 *Nitration of Paraffins.*—Nitrogen peroxide can be employed for the catalytic vapor-phase nitration of paraffins. The reactants are passed through a phosphorous pentoxide drier to a reactor maintained at 200 to 350° which is packed with fragments of glass containing oxides of arsenic or antimony or sodium salts of their oxyacids.[1] The condensed exit gases consist of nitroparaffins, dissolved nitrogen peroxide, small amounts of nitric acid, and oxidation products of the paraffins.

When a gas mixture containing 30 per cent isobutane and 70 per cent *n*-butane is reacted with two volumes of nitrogen peroxide at 200°, with a contact time of 120 sec., the yield of nitroparaffins on a weight basis is as follows:

Tertiary mononitroisobutane	60 %
2-Nitrobutane	20 %
2, 3-Dinitrobutane	20 %

The per-pass yield of tertiary nitroparaffin obtained from the isobutane is 90 per cent, or 95 per cent of isobutane consumed. The per-pass yield of secondary nitroparaffins is 25 per cent, or 90 per cent of the butane consumed.

Photochemical NO_2 *Nitration.*—The photochemical reaction of NO_2 (and N_2O_4) with benzene and nitrobenzene in the liquid and gas phases results in the formation of nitrobenzene and dinitrobenzene, respectively.[2] In all cases, photochemical activation of the reaction takes place only in the wave-length region producing excitation of the NO_2 molecules. In this electron state, NO_2 is chemically active and reacts with both benzene and nitrobenzene. The maximum yield of nitrobenzene is about 100 per cent at 55 to 60°C. in the 4,000 to 7,000 *A* region. The maximum yield of dinitrobenzene is obtained in the 1,800 to 2,900 *A* region. It appears that through the action of light the electron atmosphere of NO_2 is distorted to produce the chemically active 

V. MIXED ACID FOR NITRATIONS

Discussion.—The nitrating acid best suited for the preparation of each nitro compound should be the subject of thoughtful consideration. It is apparent, for example, that mononitrations may be carried out with more dilute acids and under milder conditions of temperature than are required for polynitro compounds. Moreover, the nitration of the former may be made with only a slight excess (0.2 to 2 per cent) of nitric acid in the mixed acid; whereas in the preparation of the higher nitrated compounds, the nitric acid content of the spent acid ranges from 3 to 10 per cent.

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[1] Levy, U. S. 2,382,241 (1945); 2,394,315 (1946).

[2] Gorislavets, *J. Phys. Chem.* (*U.S.S.R.*), **17**, 102 (1943).

In considering the composition of mixed acids, it is necessary to arrive at an understanding regarding the relationship of the three constituents HNO_3, H_2SO_4, and H_2O. For example, if the total acidity or water content of a mixed acid is kept constant and H_2SO_4 is replaced by HNO_3, it would appear possible under such circumstances to maintain a definite excess of HNO_3 to organic compound and to nitrate progressively increasing quantities of material. Accompanying the replacement of H_2SO_4 by HNO_3 under such conditions, there will be a proportionate increase in the water of reaction and a corresponding decrease in the ratio of H_2SO_4 to H_2O at the close of nitration. Since excessive dilution of the nitric acid at the end of a run is conducive to incomplete nitration and loss of volatile organic compounds, such a practice is productive of low yields of nitro compound. If, on the other hand, HNO_3 is similarly replaced by H_2SO_4, the same total acidity and nitric acid ratio to the organic compound being still maintained, it is obvious that the productive capacity of the nitrator will be diminished and a larger amount of spent acid will be produced.

It appears advisable, therefore, to formulate the composition of the mixed acid so that a definite optimum relationship exists at the close of nitration between the sulfuric acid and water. This relationship is usually termed the *dehydrating value of sulfuric acid* (*D.V.S.*).[1] It is expressed numerically by the quotient obtained by dividing the actual sulfuric acid content of the mixed acid by the total water present when nitration is completed. The latter figure includes, in addition to the water of reaction, the water that is introduced with the mixed acid and organic compound.

If, for example, a mixed acid of the following composition is used for the nitration of benzene, the dehydrating value of sulfuric acid may be calculated as follows:

$$\text{Composition of mixed acid}\left\{\begin{array}{lcr} H_2SO_4 & = & 60\% \\ HNO_3 & = & 32\% \\ H_2O & = & 8\% \end{array}\right.$$

$$\text{Mol. wts.}\left\{\begin{array}{ccccccccc} \text{Benzene} & + & \text{nitric acid} & \rightarrow & \text{water} & + & \text{nitrobenzene} \\ 78 & & 63 & & 18 & & 123 \end{array}\right.$$

When molecular proportions of acid and hydrocarbon are used, the water formed per 100 lb. of mixed acid (32 per cent HNO_3) will be

$$\frac{63}{18} : \frac{32}{X} \qquad X = 9.14 = \text{water of nitration}$$

---

[1] In some chemical plants, this relationship is called *spent acid concentrations*.

To this must be added the water that already exists in the mixed acid.

$$\text{D.V.S.} = \frac{\text{actual } H_2SO_4 = 60}{9.14 + 8} = 3.50$$

The calculations in terms of hydrocarbons are

$$\frac{78}{63} = 1.238 = \text{factor hydrocarbon to } HNO_3$$

$1.238 \times 32 = 39.62$ = pounds of hydrocarbon to be used per 100 lb. of mixed acid containing 32 per cent HNO_3.

$$\frac{78}{18} : \frac{100}{X} \qquad X = 23.08 = \text{water of nitration per 100 lb. hydrocarbon}$$

$$23.08 \times \frac{39.62}{100} = 9.14 \text{ lb. water of nitration per 100 lb. of mixed acid}$$

In actual practice, the relationship between hydrocarbon and nitric acid is worked out in advance, and allowance is made for the presence of an excess over theory of HNO_3 during nitration. The calculations may be made with reference to either hydrocarbon or nitric acid, thus: When 95 per cent of the theoretical hydrocarbon is used, the hydrocarbon factor is

$$\frac{C_6H_6}{HNO_3} = \frac{78}{63} = 1.24 \div 1.05\% = 1.18 = \text{hydrocarbon factor}$$

$$1.18 \times \%HNO_3 \text{ in } M/A^* \ (32) = 37.76 = \text{lb. of hydrocarbon per 100 lb. } M/A$$

$$\text{Water of nitration per 100 lb. hydrocarbon } \frac{78}{18} : \frac{100}{X} = 23.08$$

$$\frac{37.76 \times 23.08}{100} = 8.71 = \text{water of nitration per 100 lb. mixed acid}$$

The same results are obtained by making the calculations with reference to a nitric acid ratio; thus, if instead of a 95 per cent hydrocarbon ratio, a 105 per cent nitric ratio is used:

$$\text{Ratio } HNO_3 \text{ to hydrocarbon } \frac{63}{78} = 0.808 \times 105\% = 0.848$$

$$\frac{\text{Per cent } HNO_3 \text{ in mixed acid} = 32}{HNO_3 \text{ ratio to hydrocarbon} = 0.848} = 37.74 \text{ lb. of hydrocarbon per 100 lb. mixed acid of } 32\% \ HNO_3 \text{ content}$$

$$\text{D.V.S.} = \frac{\text{actual } H_2SO_4 \text{ in } M/A = 60}{H_2O \text{ of nitration, } 8.71 + \text{water in } M/A, 8} = 3.59$$

The control of the D.V.S. is a matter of great practical importance in maintaining high efficiencies in nitrating operations. In the nitration of benzene, for example, when acids of the following compositions were used, (I) would often show the presence of unnitrated benzene and generally gave lower yields in spite of the fact that the total acidities are the same.

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* M/A = mixed acid.

(I) D.V.S. 2.96 %		(II) D.V.S. 3.51 %
54.0	H_2SO_4	60.0
38.0	HNO_3	32.0
8.0	H_2O	8.0

Use of Cycle Acid in Nitration.—The term *cycle acid* is used to describe that portion of the spent acid from nitrations which is used over again in ensuing operations. The use of cycle acid, which is essentially diluted sulfuric acid, in starting a nitration is merely another phase of the well-founded practice of using mixed instead of straight nitric acid. From experience, it had been found that the use of an acid having approximately the same composition as that naturally formed in the reaction would accentuate the smoothness of reaction and furthermore introduce a factor of safety by causing the organic compound to come in contact first with dilute sulfuric acid and then gradually with the stronger nitrating acid that was delivered to the nitrator. The approximate composition of spent acid from the mononitration of benzene is as follows:

H_2SO_4	80 to 85%
HNO_3	3 to 0%
H_2O	17 to 15%

The principle underlying the use of cycle acid is based on the fact that, compared with cycle acid, the concentrated sulfuric and nitric acids employed for nitration possess a high integral heat of dilution and comparatively low heat capacity.[1] This accounts for the difficulty in controlling nitrating operations at the start and the fact that the reaction runs smoothly as soon as some of the nitric acid is replaced by the water of nitration. The problem of temperature control is thus simplified by the use of cycle acid which quickly absorbs the heat developed and transfers it to the cooling system that is provided.

Heat Capacity of Sulfuric Acid (15°C.)

Sp. gr.	H_2SO_4, %	Specific heat	Sp. gr.	H_2SO_4, %	Specific heat
1.841	98.5	0.33	1.71	77.5	0.41
1.839	95.0	0.34	1.61	69.0	0.45
1.820	90.0	0.36	1.53	62.5	0.49
1.77	83.4	0.38	1.45	55.0	0.55

The method of nitrating with cycle acid is consequently characterized by the introduction into the nitrator of a considerable weight of material, inert as far as conditions of nitration are concerned. This would be a serious handicap if provisions were not made systematically to remove this diluent from the vessel. The withdrawal of cycle acid is termed *bleeding* the nitrator, and this acid resulting from the bleeding process is, of course, subsequently returned to the nitrator.

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[1] Rhodes and Nelson, *Ind. Eng. Chem.*, **30**, 648 (1938).

Use of Cycle Acid Fortified by Nitric Acid.—During the nitration process using mixed acids calculated to complete the reaction in a satisfactory manner, there is a continuous diminution in the HNO_3 content and increase in the H_2O content. The composition of the mixed acid at any stage in the process can, of course, be readily calculated. It is important, however, to remember that the mixed acid, although undergoing continuous dilution, is an excellent nitrating agent for the conditions that prevail during intermediate points.

Assume the employment of a satisfactory nitrating acid *A* which will yield spent acid *C* after nitrating ½ mole of hydrocarbon per 100 gm. of *M/A*; the former will give up 31.5 gm. HNO_3 and will gain 9 gm. H_2O during the process. At 80 per cent completion, the nitrating acid will have composition *B*, which, of course, is capable of satisfactorily converting the residual hydrocarbon to nitro derivative. When used in a system designed to remove the water of nitration in a continuous and integrated manner, such "intermediate" acids possess a number of advantageous characteristics:

	A Nitrating acid, initial composition	*B* Intermediate acid at 80 % completion	*C* Spent acid, % composition
H_2SO_4	59.0	77.0	81.5
HNO_3	32.5	7.3	1.0
H_2O	8.5	15.7	17.5
	100.0	100.0	100.0

1. They have a relatively high heat capacity, *i.e.*, low integral heat of dilution (see following paragraphs).
2. It is relatively easy to dissipate the small prevailing heat of reaction in the large body of nitrating acid.
3. There is no danger of overheating leading to explosive, oxidative chain reactions. A short nitration time is thus made practical.
4. Rapid feeding of reactants is feasible; and, instead of cooling being necessary, the spent acid is deliberately kept warm to facilitate the subsequent removal of the water of nitration.

These considerations have led to the use of a spent acid fortified with nitric acid for the continuous nitration of benzene and other compounds (see technical section). In such operations, relatively small quantities of hydrocarbon are subjected to reaction with relatively large volumes of spent acid—still possessing dehydrating properties—which are fortified by the addition of aqueous nitric acid. Provision is made, however, for the integrated and continuous removal of the water increment.

Thermal Properties of Nitrating Acids. *Heats of Dilution.*—In the nitration of a hydrocarbon by means of a mixture of concentrated nitric and sulfuric acids, the total heat liberated is equal to the heat of solution of the initial mixed acid minus the heat of solution of the final spent acid minus the heat of solution of the nitric acid entering into reaction plus the heat of the nitration reaction. Although heats of nitration are relatively large, the control of the reaction is intimately related to the heats of dilutions of the nitrating acid.

The heats of dilution of mixed acids that contain various known percentages of sulfuric acid, nitric acid, and water were measured by Rhodes and Nelson, and their data are represented graphically in Fig. 4.[1] The curves show in an impressive manner the pronounced lowering of the heats of dilution as the nitration progresses and the water content of the nitrating acid increases. It is clear that at the start of the reaction, the total heat liberated per unit of nitro compound formed is relatively great. Furthermore, owing to the lower specific heats of the more concentrated acids (see Fig. 5), there is greater danger of violent or explosive reactions during the early stages of nitration.

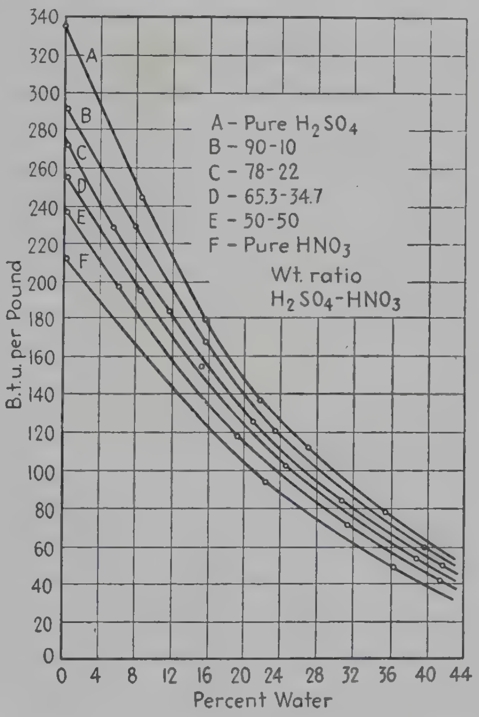

FIG. 4.—Heats of dilution of mixed acid. Points on these curves indicate the heat of dilution per pound of acid of indicated $H_2SO_4 - HNO_3$ weight ratio, containing the percentage water shown on abscissa. Heat evolved during actual nitration can be computed from data pertaining to composition of acids at beginning and end of reaction.

The curves of Fig. 4 indicate quite clearly why it is comparatively safe to make rapid nitrations at relatively high temperatures with spent acid fortified with nitric acid or with nitric acid alone. The nitrating acids with lower heats of dilution and high heat capacity have an added economic advantage in that smaller quantities of heat are necessary for the removal of the water of nitration in integrated system.

Integrated Heats of Nitration.—McKinley and Brown have developed an enthalpy chart (Fig. 5) whereby the thermal properties of mixed acids

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[1] RHODES and NELSON, *Ind. Eng. Chem.*, **30**, 648 (1938).

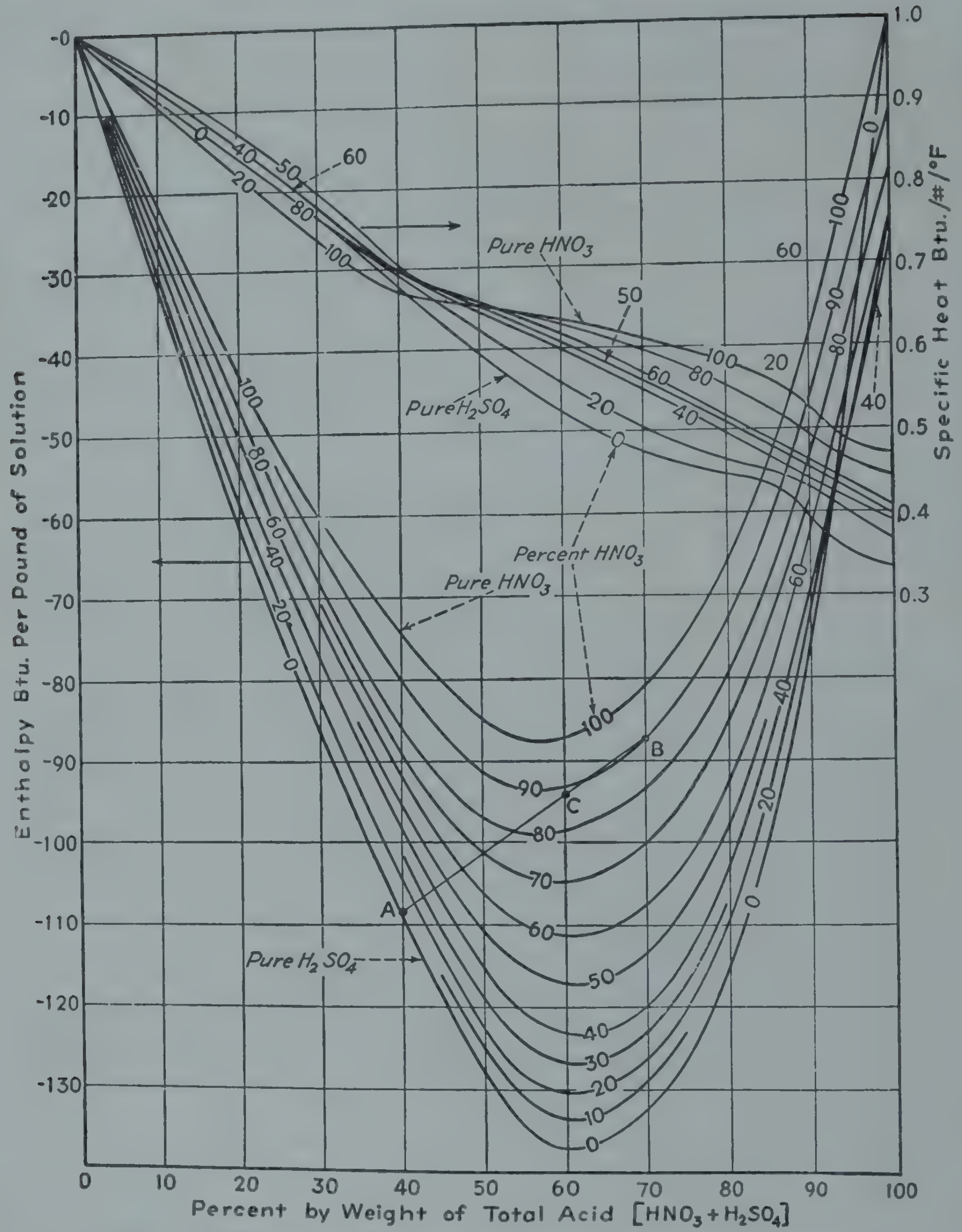

Fig. 5.—Enthalpy of nitric acid, sulfuric acid and water mixtures.[1]

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[1] The ordinate of Fig. 5 is enthalpy in "B.T.U. per pound of solution" and its abscissa is "per cent by weight of total acid in mixed acid solution." The enthalpy for a specific composition is obtained by interpolation between the lines of *indicated nitric acid composition*, being based on anhydrous $HNO_3 + H_2SO_4$. For example, the line of 60 per cent HNO_3 on the above plot represents the enthalpy at 32°F. of all mixtures of water with an acid containing 60 parts nitric acid to 40 parts sulfuric acid on the basis of anhydrous acid ($HNO_3 + H_2SO_4$).

are made readily available for calculating heat balances in nitration operations.[1,2] Plotted in Fig. 5 against the same abscissa but against different ordinates are the specific heat data for the system. From this figure, containing both 32°F. relative enthalpies and specific heats, the enthalpy of any liquid mixture of nitric acid, sulfuric acid, and water can be readily calculated by reading the desired relative enthalpy at 32°F. and the specific heat from the chart.

The type of information that can be obtained graphically by using the enthalpy chart is illustrated by the following example:[3]

1. Find the relative enthalpy of a mixed acid of the following composition at 90°F.:

HNO_3	30 %
H_2SO_4	20 %
H_2O	50 %

$\%HNO_3$ on anhydrous or water-free basis $= \frac{30}{50} \times 100 = 60\%$

% total acid = 50 %

Then read from the chart at 50 per cent on the abscissa and at 60 per cent on the per cent HNO_3 line $\cdot H = -106$ B.t.u. per lb. of solution and specific heat = 0.66 B.t.u. per lb. of solution per °F.

$$H_{90^\circ} = -106 + (90 - 32)(0.66) = -67.7 \text{ B.t.u. per lb.}$$

The heat to be removed per 100 lb. of mixed acid in technical nitrations can readily be computed in the same manner.

VI. FACTORS AFFECTING NITRATION

Influence of Nitration Temperature.—In contradistinction to sulfonation, the nitrating temperature has comparatively no directive influence on the position taken by the entering —NO_2 group, but it is of importance in controlling the purity of the reaction product. With ascending temperatures, the degree of nitration is increased so that a proportional amount of a higher nitrated product is formed. The deleterious influence that such impurities may exercise in subsequent operations is apparent. Nitric acid is furthermore a good oxidizing agent, its activity becoming more pronounced at higher temperatures. Part of the raw material may thus be converted into valueless products which not only lower the direct yields but also make purification of the nitro compound imperative. The presence of sulfuric acid, along with red oxide of nitrogen (NO_2), tends to the formation of nitrosylsulfuric acid, a compound possessing strong oxidizing properties, which may also cause oxidation when the

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[1] McKinley and Brown, *Chem. Met. Eng.*, **49**, 142 (1942).

[2] The enthalpy (formerly called the *total heat* or *heat content*) of a unit weight (1 lb.) of a substance in B.t.u. per pound is here the algebraic sum of the thermal factors entering into the production and use of mixed acids for nitration processes. Standard state, 32°F.

[3] McCurdy and McKinley, *Ind. Eng. Chem.*, **34**, 1002 (1942), have developed a convenient nomograph for some of these calculations.

dehydrating strength of the mixed acid is low. It is therefore of the greatest importance, especially when nitrating a compound that is easily oxidized, to keep the temperature sufficiently low to prevent this action. Oxidation is accompanied by the development of nitrogen oxides, which may cause further complications in case the material being nitrated will react with nitrous acid. Included in this category are amino compounds which may first be converted to diazo compounds and subsequently to hydroxy compounds; also, the alkylated amino compounds and hydroxy compounds which are able to form nitroso compounds by the action of nitrous acid. For this reason, it is advisable to protect amino and hydroxyl groups by converting them into their acetyl compounds by means of glacial acetic acid. Formic acid and benzaldehyde may also be used for this purpose; but for economic reasons, they have not been widely adopted. If the nitrated acyl compound is hydrolyzed, the desired nitro derivative is obtained.

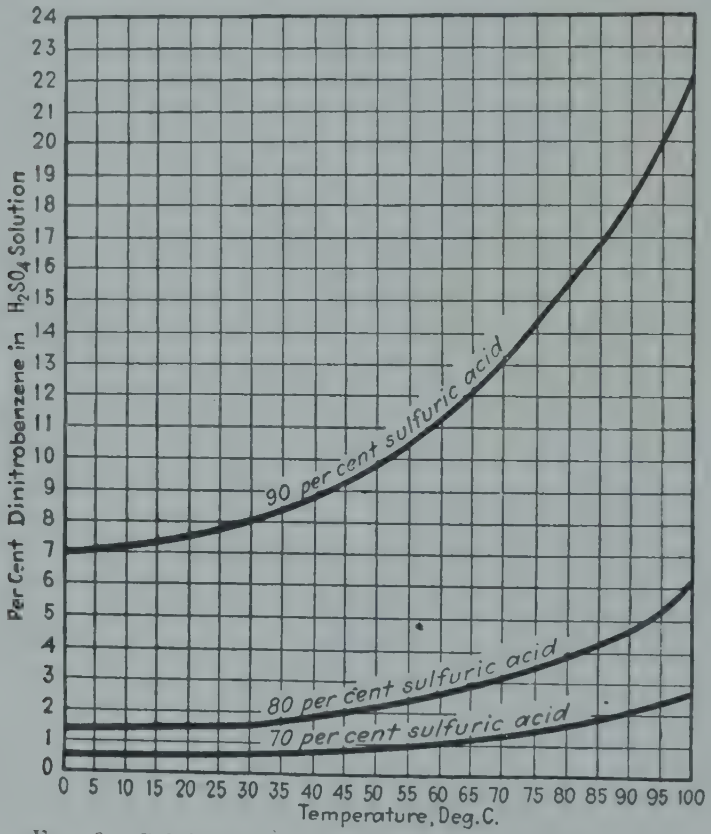

FIG. 6.—Solubility of dinitrobenzene in sulfuric acid.

Agitation.—According to Lewis and Suen, the nitration reaction goes on in both the acid and organic phases.[1] By emulsification each phase can be kept saturated with the other, and under these conditions, other things being equal, the rate in each phase is constant, that in the acid phase being several fold the rate in the organic phase. If the interfacial surface of contact between the phases is limited in amount, as by reducing the amount of organic compound (benzene) emulsified in the acid or by avoiding emulsification, reaction rate drops rapidly because diffusion is no longer sufficient to keep each phase saturated with the reacting component from the other phase. This reduction in reaction rate conforms quantitatively to the assumption that diffusion has now become the controlling factor. No indication whatever of localization of the reaction at the interface is found.

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[1] LEWIS and SUEN, *Ind. Eng. Chem.*, **32**, 1095 (1940).

Solubility.—The solubility of the nitro compounds in sulfuric acid is another factor of primary importance. The increase in solubility with rise of temperature and decrease with dilution of the acid are shown in Fig. 6 for dinitrobenzene. Since nitro compounds are more soluble in the more concentrated sulfuric acid, a mixed acid of high H_2SO_4 concentration increases the speed of arrival at the eventual degree of nitration. The effect that the sulfuric acid content has on the speed of dinitration of nitrobenzene is shown by the curves of Fig. 7. Here the fractional consumption of nitric acid plotted against the reaction time is shown.[1]

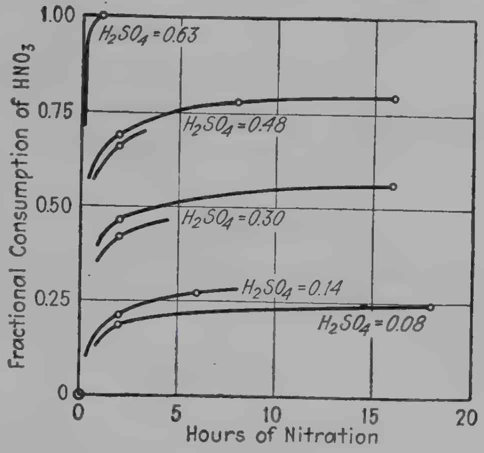

FIG. 7.—Speed of consumption of nitric acid in certain nitrating acids with the molar fractions of H_2SO_4 shown.

VII. EQUIPMENT FOR NITRATIONS

Nitrating Apparatus.—Most nitrations are carried out in closed iron vessels that are provided with an agitating mechanism and means for controlling the reaction temperature. Nitrators are usually constructed of acid-resisting cast iron and steel, but often acid-resistant alloys, particularly chrome-nickel steel alloys, are used. These vessels may be obtained in sizes ranging from 1-gal. capacity for laboratory use to 1,600-gal. or more capacity for economical industrial operations. Most of the tools provided by equipment manufacturers possess valuable characteristics that make each one particularly useful for a definite set of conditions. Three types of apparatus are discussed in these pages in order to provide a basis for studying the two essential attributes of a safe and efficient nitrator: heat exchange and agitation.

When temperature regulation is dependent solely on external jackets, a disproportional increase in nitrator capacity as compared with jacket surface occurs when the size of the machine is enlarged. Thus, if the volume is increased from 400 to 800 gal., the heat-exchange area increases as the square and the volume as the cube of the expanded unit. To overcome this fault, internal cooling coils and tubes are introduced, and these have proved satisfactory when installed on the basis of sound calculations that include the several thermal factors entering into this unit process.[1]

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[1] HETHERINGTON and MASSON, *J. Chem. Soc.*, **1933,** 109.

The necessity for providing an efficient agitation inside the nitrator is of great importance. Reference has already been made to the increased reaction velocity resulting from a more efficient agitation. Of equal importance is the fact that, in a properly designed apparatus, local overheating at the point where the acid and organic compound first make contact is avoided and a safer operation is ensured. Furthermore, the smoothness of the reaction depends on the dispersion of the reacting material as it comes in contact with the charge in the nitrator so that a fairly uniform temperature is maintained throughout the vessel.

Nitrators are usually equipped with one of three general types of agitating mechanism. These may be designated as (1) single or double impeller; (2) propeller or turbine, with or without sleeve; and (3) outside tunnel circulation. Reproductions of such vessels along with pertinent operating data are given on following pages.

The *single-impeller* agitator consists of one vertical shaft containing horizontal arms. The shaft may be placed off center in order to create rapid circulation past or local turbulence at the point of contact between the nitrating acid and the organic compound.

The *double-impeller* agitator consists of two vertical shafts rotating in opposite directions. To each shaft is attached a series of horizontal arms. The lower blades have an upward thrust, whereas the upper ones repel the liquid downward. The contents of such nitrators are practically homogeneous. The volume increases as the nitration progresses; and in such vessels it is not advantageous to use cycle acid, for it cannot be drawn off.

The term *sleeve-and-propeller* agitation is usually applied when the nitrator is equipped with a vertical sleeve through which the charge is circulated by the action of a marine propeller or turbine. The sleeve is usually made of a solid bank of acid-resisting cooling coils through which cold water or brine is made to circulate at a calculated rate. In order to obtain the maximum efficiency with this type of nitrator, it is essential to maintain a rapid circulation of liquid upward or downward in the sleeves and past the coils. Obtaining the desired velocity of the liquid is a matter of regulating the speed of the propeller used.

When aromatic hydrocarbons are being nitrated, the nitrating acid is generally fed into the spent or cycle acid by means of an annular acid distributor placed a few inches directly under the revolving propeller (Fig. 9). If the mixed acid is delivered into the cycle acid, the nitration is made with a fortified spent acid, and this practice is conducive to a better control of temperature. In the nitration of polyhydric alcohols, the organic compound may be distributed over the charge and then drawn or beaten into the acid, which may be either a concentrated mixed acid or a fortified cycle acid.

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[1] Reference to works on *unit operations* in chemical engineering is valuable for such studies (see WALKER, LEWIS, and MCADAMS, "Principles of Chemical Engineering"; also BADGER and MCCABE, "Elements of Chemical Engineering").

When benzene or toluene are nitrated in the sleeve-and-propeller type of nitrator, two distinct layers of liquid are maintained throughout most of the nitration—a lower one of spent acid and an upper one consisting of hydrocarbon and nitrohydrocarbon. As the propeller forces the cycle acid, which has been fortified by the addition of mixed nitrating acid, through the sleeve, it attacks a portion of the hydrocarbon layer without breaking the surface. As nitration nears completion, the specific gravity of the cycle acid decreases and the nitrated hydrocarbon increases to approximately the same density, after which the two liquids are uniformly mixed by the agitation but separate very rapidly when agitation is discontinued.

A syphon or overflow system is used to maintain constant level in the nitrator. The withdrawal of the cycle acid is generally made from the bottom of the nitrator, as near the center as is possible. The amount of hydrocarbon carried off through the bleeding system is governed by the following factors: (1) speed of agitation; (2) distance of propeller from the bottom of the nitrator; and (3) the shape of the bottom of the nitrator.

The most satisfactory results may be obtained by running the propeller at a speed that ensures turning the charge over from two to three times per minute and placing the propeller at such a distance from the bottom of the nitrator that very little agitation occurs at the bottom level of the cycle acid. A cone-shaped nitrator bottom or one having a deep well at the base is undoubtedly the most practical; for in this way, a dead pocket of cycle acid would be formed, thus eliminating the probability of a large amount of hydrocarbon being carried off with the cycle acid.

Outside Tunnel Circulation.—Agitation brought about by circulating the cooled nitrator charge through outside tunnels is a characteristic of the *Hough nitrator*. This nitrator is built with two tunnels, one on either side of the body of the nitrator. There are two impellers revolving at from 200 to 400 r.p.m., according to the size of the machine. In this type, the contents of the nitrator are completely circulated once each minute, the rate of circulation of the liquid through the tunnels in a large-size machine being about 2,500 gal. per min.

Well down the tunnels and under the impellers is the injector for the hydrocarbon to be nitrated and for the nitration acid. The latter is forced in a small stream into the benzene-cycle acid mixture so that approximately 1 lb. of incoming nitrating acid comes in contact with 1,000 lb. of material in the nitrator. This is a desirable condition to obtain in nitration and prevents any local rise of temperature.

By referring to the drawing of this machine (Fig. 8), it will be seen that the circulation of the liquid is from the lower part of the tunnel over the port and into the body of the machine. Obviously, in order to function properly, the ports must be covered at the start with a liquid heavier than the hydrocarbon or substituted hydrocarbon to be introduced. The cycle acid system of nitration brings this condition about in an ideal manner.

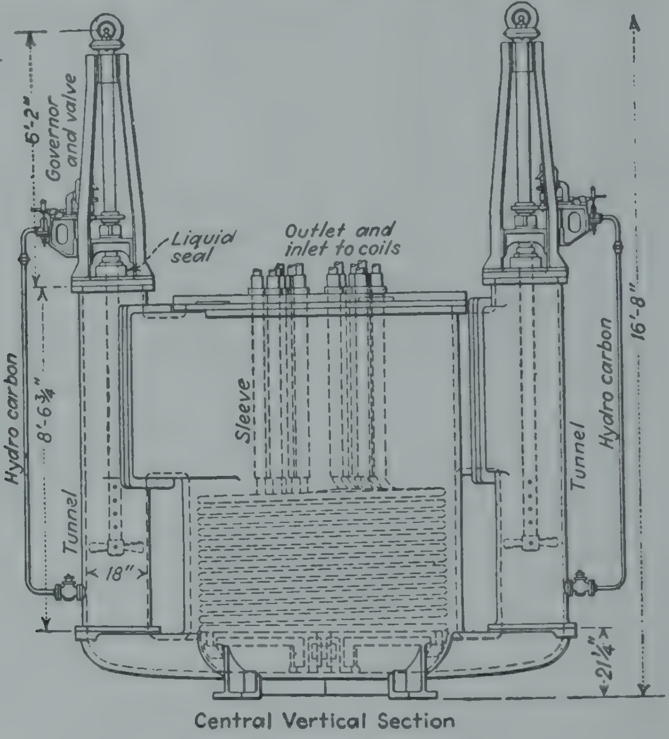

FIG. 8.—Hough nitrator, cast iron, with external tunnels.

For the first run of the nitrator, a charge of sulfuric and nitric acid corresponding to the normal spent acid obtained from the nitration must be prepared. This acid is placed in the nitrator so as to cover and just overflow the ports of the machine. The agitator (impeller) is now started up, and the whole of the benzene charge is run into the machine through the injector pipes at the side of the tunnels. It is quite immaterial how fast it is run in, as the agitation is efficient, and the amount of nitric acid in the cycle acid so small that practically no elevation of temperature occurs. As soon as all the benzene is in, the nitrating mixed acid is forced in through the injector pipes, keeping the temperature within the desired limit. It is quite possible to conduct a run in this way at a temperature of 60°C., without the least danger of the temperature's rising beyond control. After all the nitrating acid has been added, the temperature may be held at 90°C. for 2 hr. to complete the reaction.

The withdrawal of the original cycle acid is started at the moment the nitrating acids are being added. Just as much cycle acid is drawn from the nitrator as nitration acid is added, the volume in the nitrator being maintained practically constant. The withdrawal of the cycle acid is done from a cock placed at the lowest point of the nitrator, where there is least agitation. A very small amount of nitrobenzene, of course, is carried along with the cycle acid. The acid collected from the *bleeding* process is subsequently returned to the nitrator; fresh benzene is added and then nitrated in the manner previously described.

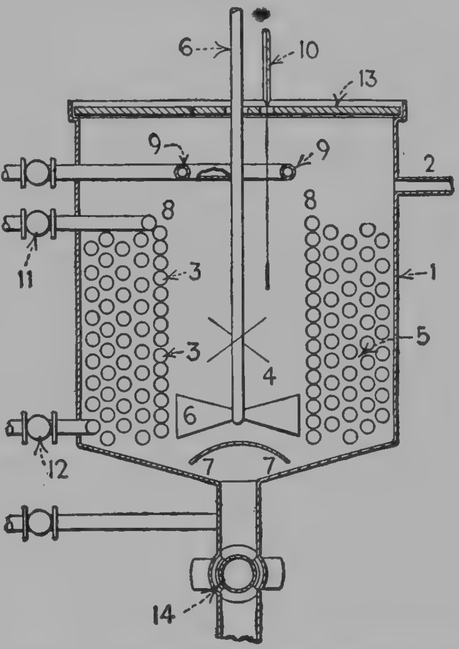

Fig. 9.—Nitrator with banked coils for continuous or batch nitrations.

Continuous Nitrations.—The apparatus shown in Fig. 9 may be employed for both batch and continuous operations.[1] The nitrator comprises two compartments, an inner mixing chamber 4 surrounded by a solid bank of cooling coils 3 and an outer cooling zone 5 containing an elaborate system of cooling coils.

In the nitration of polyhydric alcohols, the vessel is charged with sufficient cycle acid just to overflow through pipe 2, and the concentrated nitrating acid is admitted at the lower portion of the vessel under the distributor baffle 7. The stirrer causes the fortified acid mixture to travel upward through the outer cooling chamber; and as it flows over the coils at 8 it receives the polyhydric alcohol, *e.g.*, glycerol or glycol, which is delivered through the distributor pipe 9.

The heat of reaction is taken up by the precooled acid, and therefore no appreciable rise in temperature occurs in the reaction zone. The passage of the charge downward through the inner mixing chamber is sufficiently rapid, and the reaction mixture is quickly forced into the dense network of cooling coils in the cooling chamber. Because the mixing zone is free of pockets or obstacles, there is a thorough incorporation of the newly formed nitro compound, and local temperature differences do not arise.

[1] U. S. 1,893,447 (1933).

When polyhydric alcohols are to be nitrated in a continuous manner, a quantity of the reaction mixture corresponding to the quantity of reactants introduced is run off through the overflow pipe 2, this outlet maintaining a practically constant level of liquid during nitration. Since the reaction temperature is practically constant and uniform throughout the process, there is a possibility that the yields of organic nitrate may not be so high as that obtained in batch operations wherein the temperature is slightly raised at the close of the operation to ensure complete nitration. The nitrator is emptied through connection 14 at the base when operations are suspended.

This system may be employed for nitrations in general, since the circulation of the charge can readily be directed up or down in the mixing chamber and the nitrating acid and organic compound may be admitted through any suitable connections.

For the nitration of hydrocarbons, it is desirable to equip the propeller with emulsifying vanes and to ensure the admission of air into the free space in the nitration. The air drawn into the mixing chamber serves to disperse the drops of hydrocarbon, *e.g.*, toluene delivered by distributor 9, and thus facilitates nitration.[1]

Instead of conventional equipment being used, the nitration reaction can be carried out *continuously* by flowing a thin film of benzene (or other hydrocarbon) under gravity down the inner surface of a vertical tube and hurling a solution of mixed acid into such a film. The resultant surface mixture passes down a sufficient length of tube to permit substantial or complete nitration while the liberated heat is removed by cooling fluids on the outer surface of the tube.[2] The products of reaction which separate into two sharply defined layers are collected at the base of the tube. The upper organic layer is decanted, washed, and distilled to give a yield of 91 per cent nitrobenzene.

VIII. TECHNICAL NITRATIONS

General Remarks Regarding the Technical Preparation of Intermediates.—The following paragraphs present methods for the production of some of the more important nitro compounds. In these syntheses, as in the other technical operations described in this volume, the heavy chemicals used are the usual high-grade technical quality. The cyclic hydrocarbons or their derivatives are generally purchased in quantity by contract according to well-defined specifications regarding their physical properties and chemical behavior. It is common practice to analyze samples of each shipment received, and these analyses form the basis for subsequent yield calculations. It is customary in chemical plants to take stock of all materials monthly and to calculate the yields obtained, the latter being usually expressed as pounds of finished product per 100 lb. of raw material used.

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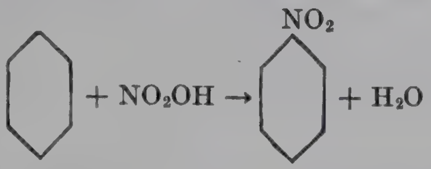
[1] Brit. 455,570 (1935).

[2] Waterman *et al.*, U. S. 2,217,263 (1940).

PREPARATION OF NITROBENZENE



In the following paragraphs, a study will be made of some of the more important details of nitrobenzene manufacture in order that the observations may be of value in the preparation of the other nitro compounds that will later be described.

Batch Nitration with Mixed Acid.—The description that follows assumes the use of cycle acid, although this practice is neither general nor essential, particularly when the problem of heat transfer has been satisfactorily solved. The operation commences by delivering to the nitrator sufficient cycle acid, *i.e.*, spent acid from a previous charge in which some nitrobenzene and nitric acid are still present. The amount of such acid required depends on the type of nitrator used. In the sleeve-and-propeller type, it must cover the propeller; and in the Hough nitrator, it must cover and overflow through the ports of the machine. Cold water is then circulated through the heat-exchange medium; and when the temperature is 50°C. or lower, the charge of benzene is pumped from the scale tank into the nitrator.

The mixed acid for nitration can be fed on top of the hydrocarbon or under the surface. When top feed is used, there is always a slight loss of benzene vapors due to the reaction with surface hydrocarbon accompanied by the local evolution of heat. When undersurface feed is used in conjunction with paddle-type agitators, the acid runs into a lead funnel placed on the agitator just above the top paddle. A lead pipe leads from the funnel to one of the lower paddles, where it makes a loop upward. The loop in the lead pipe is always full and prevents spluttering, as the mixed acid now comes in contact with the cycle acid at the lower part of the nitrator instead of making direct contact with benzene. A similar feeding arrangement is made for the sleeve-and-propeller type of machine by terminating the lead pipe just under the propeller. In the Hough nitrator, this is all taken care of in the design of the machine, as the mixed acid is forced in a small stream into the benzene-cycle acid mixture.

The temperature of nitration for benzene may vary within fairly wide limits. When no cycle acid is used, it is inadvisable to exceed 50°C.; but when fortified spent acid is employed, the nitration temperature may be kept between 50 and 55°C. The efficiency of agitation and heat exchange are also important considerations, which affect not only the control of temperature but also the rate of feed.

To arrive at the proper amount of mixed acid to be used per charge, it is necessary to multiply the weight of benzene by the acid factor that is used in making the calculations for the D.V.S. (see page 25), provision being made for the presence of a slight excess of nitric acid.

Separation and Neutralization.—The separation and neutralization of the nitrobenzene are accomplished in large conical-bottomed lead tanks, each capable of holding one or more charges. The nitrator charges are permitted to settle here for approximately 12 hr., when the spent acid is drawn off from the bottom of the lead tanks and delivered to the spent acid tanks for additional settling or for treatment with benzene next to be nitrated, in order to extract the residual nitrobenzene. The nitrobenzene is then delivered to the neutralizing house.

The neutralizing tub may be either a large, lead, conical-shaped tub containing an air spider, which is used for agitating the charge of nitrobenzene during the washing process, or a standard cast-iron kettle similar to the nitrator with sleeve-and-propeller agitation. The neutralizing vessel is prepared with a "heel" of warm water, which is delivered from an adjacent vat, and the nitrobenzene is blown into it. The charge is thoroughly agitated and warmed with live steam for 30 min. and then allowed to settle for a similar period. The supernatant acid water is then run off through side outlets into a labyrinth where practically all the enmeshed nitrobenzene will settle out.

The charge is now given a neutralizing wash at 40 to 50°C. with a warm sodium carbonate solution. When the nitrobenzene is intended for aniline production, this may be followed by a wash with aniline water from the reducer house if any has to be worked up. Otherwise, a final washing with a small quantity of warm water is made. The nitrobenzene is then delivered to its storage tanks where it is again settled to remove final traces of water. The crude product can now be distilled for commerce or used directly for the preparation of aniline. In some plants where the nitrobenzene is used almost exclusively in the aniline plant, the neutralizing and subsequent washes are omitted. The nitrobenzene delivered to the reducer houses is consequently acid. No harmful effects on the equipment are noticeable, provided the acidity is kept below 0.5 per cent.

Operating Losses in Nitrobenzene. *Loss in Waste Acid.*—When the nitrobenzene in the spent acid is not extracted by countercurrent washing with benzene next to be nitrated, it is recovered by permitting the acid to settle in large lead-lined vats from 8 to 24 hr., the duration depending on production schedules. The percentage of nitrobenzene removed in waste acid depends upon the temperature and efficiency of separation and is approximately 0.5 per cent of the yield. These losses are in excess of the true solubility losses (Fig. 10), being caused by incomplete separation of the nitrobenzene from the spent acid.

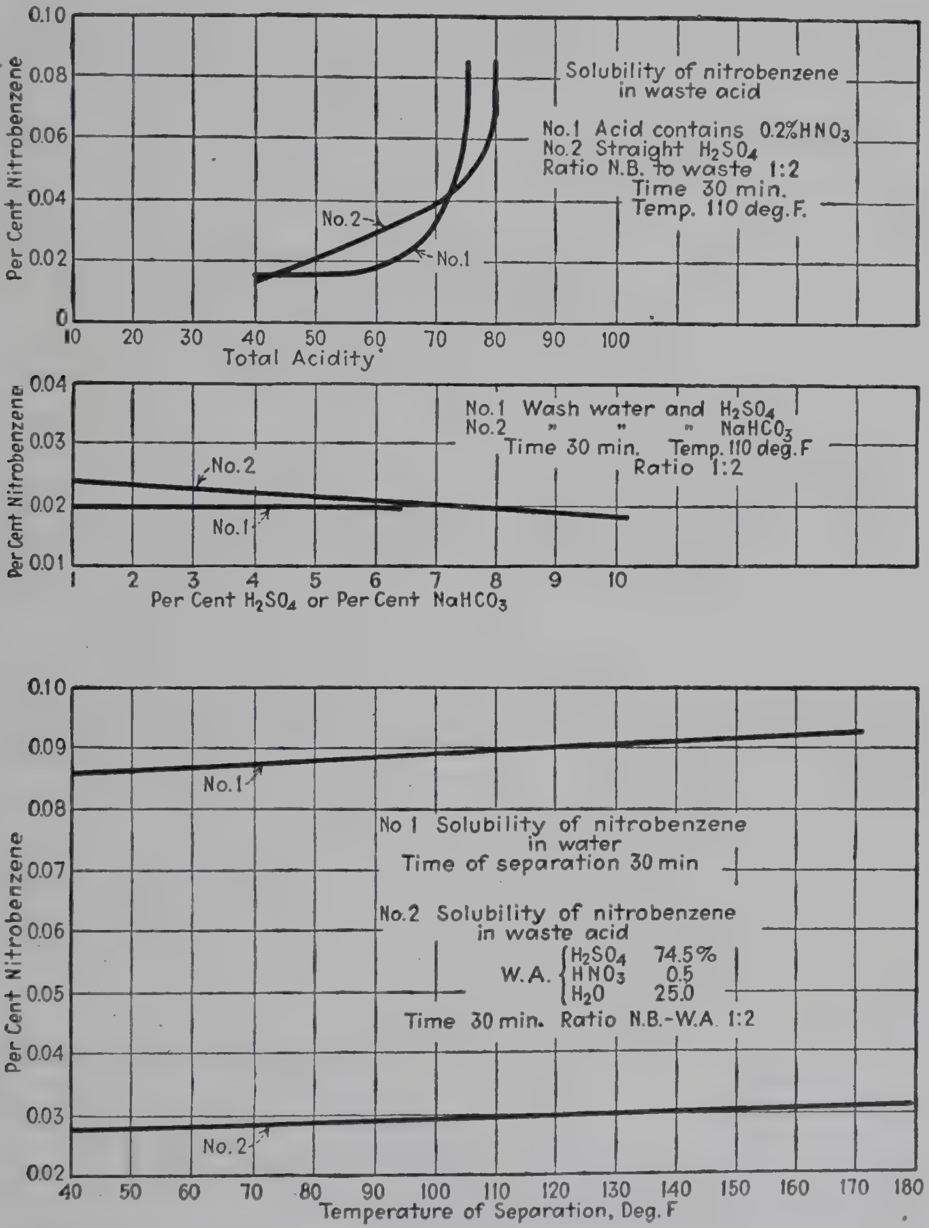


FIG. 10.—Solubility losses in neutralizing and washing nitrobenzene.

Loss in Wash Waters.—The losses incidental to the neutralization of the nitrobenzene are directly proportional to the number of washes given and the amount of water used. In neutralizing, three washes may be given, the second of which contains sodium carbonate. The washes are made at a temperature of about 45°C. and are agitated with air and steam and then permitted to settle. The wash waters are drawn off at different levels and are delivered to a series of wood catch boxes, the overflow from the last one going to waste. The quantity of nitrobenzene actually lost at this source is always slightly higher than what might be expected from the curves in Fig. 10 showing the solubility of nitrobenzene in wash waters.

NITRATION OF BENZENE: OPERATING DATA[1]

HOUGH NITRATOR

Initial charge of weak acid to represent cycle acid	9,000 lb.

Composition of above:

H_2SO_4	83.0%
HNO_3	2.3%
H_2O	14.7%

Nitric content includes low oxides of nitrogen.

Charge of benzene	10,000 lb.
Charge of mixed acid	23,300 lb.
Nitric acid ratio	1.04

Composition of mixed acid (99% acidity):

H_2SO_4	62.8%	5.7 D.V.S.
HNO_3	36.1%	
H_2O	1.1%	

Nitric content includes low oxides of nitrogen amounting to about 0.2%.
Yield of nitrobenzene[2] about 15,698 lb. = 156.9 lb. nitrobenzene per 100 lb. benzene.
Length of time required to introduce benzene into inert (cycle) acid, about ½ hr.
Time required to inject nitrating acid, 1 hr.
Time required to cook at 90°C., 2 hr. 5 min.
Total time for run, 3 hr. 35 min.

NITRATION WITH SLEEVE-AND-PROPELLER AGITATION

Charge of benzene	6,000 lb.
Time of nitration	2.5 hr.
Temperature of nitration	50–60°C.
Time of digestion or cooking at 50 to 60°C	2 hr.
Yield per 100 lb. benzene	154–155 lb.
HNO_3 in waste acid	0.3%

The above results are obtained in a closed system of nitration, using cycle acid and top feed. No HNO_3 remains in spent acid when benzene is used in excess.

COST FACTORS IN PRODUCTION OF NITROBENZENE

Nitration of benzene to nitrobenzene:

Molecular weight benzene (C_6H_6)	78
Molecular weight nitrobenzene ($C_6H_5NO_2$)	123
Theoretical yield per 100 lb. C_6H_6	157.6
Standard yield for determining costs (98% of theory)	154.5

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[1] From GROGGINS, "Aniline and Its Derivatives," D. Van Nostrand Company, Inc., New York.

[2] The above yields are based on 100 per cent C_6H_6 as used. No allowance is made for losses in handling. The nitrobenzene dissolved in the waste acid is recovered by washing, with the benzene next to be nitrated either in the nitrator or in a separate vessel.

Materials to produce 100 lb. nitrobenzene:

65.15 lb. benzene, at $0.028[1]	$1.82
71.00 lb. H_2SO_4, at $0.007	0.50
55.00 lb. HNO_3, at $0.03	1.65
1.00 lb. Na_2CO_3, at $0.012	0.01
Total material cost	$3.98

Credits:

69.0 lb. H_2SO_4 in waste acid, at .0.003	$0.21
0.9 lb. HNO_3 in waste acid, at $0.02	0.02
	$0.23
Therefore, net material cost per 100 lb. nitrobenzene	$3.75

Operating costs:	
Operating labor and direct supervision Repairs labor Repairs material Supplies	$0.15
Power costs:	
Electricity Steam Air Water Brine	0.20
Overhead:	
Administration Depreciation Insurance Fixed charges	0.52
Net cost per 100 lb. of nitrobenzene	$4.62

ANALYSIS OF NITROBENZENE COST DATA

Percentage cost analysis:[2]

	% of Total Cost
Operating cost	$\frac{0.15}{4.62} = 3.25$
Power cost	$\frac{0.20}{4.62} = 4.33$
Overhead	$\frac{0.52}{4.62} = 11.25$
Raw materials	$\frac{3.75}{4.62} = 81.17$

---

[1] Benzene at 20 cts. per gal.; add ⅛ ct. per lb. to final cost for every cent increase above 20 cts. per gal. as cost of benzene. The above figures do not include packaging, storing, or sales costs.

[2] Numerator = cost of each phase of production; denominator = total net cost.

When the nitration operations are conducted according to the methods noted on page 39, the yields range from 153 to 156.9 lb. of nitrobenzene obtained per 100 lb. of benzene used. The latter figure closely approaches the theoretical 157.6; and since each percentage increase in yield is equivalent to about a fourth of the operating cost (see cost sheet, page 43), it is a matter of great moment to maintain high operating efficiencies.

Continuous Nitration with Fortified Spent Acid.—Methods for the continuous nitration of benzene have been proposed by Castner and Mares.[1,2] Both processes are based on the recognition that a slightly HNO_3-fortified spent acid constitutes a satisfactory nitrating agent for a limited quantity of hydrocarbon. To obtain volume production, it is necessary to circulate relatively large quantities of acid of low nitric acid content and high heat capacity, and to remove the water of nitration continuously in an integrated evaporator operating under reduced pressures. When the heat of sulfuric acid hydration and the chemical heat of nitration are caused to take place in separate vessels by adding nitric acid to a prepared mixture of benzene, sulfuric acid, and water, the hazards of nitration are further reduced and it is feasible to operate safely at relatively high temperatures and to utilize the sensible heat in effecting the subsequent removal of water from the spent acid.

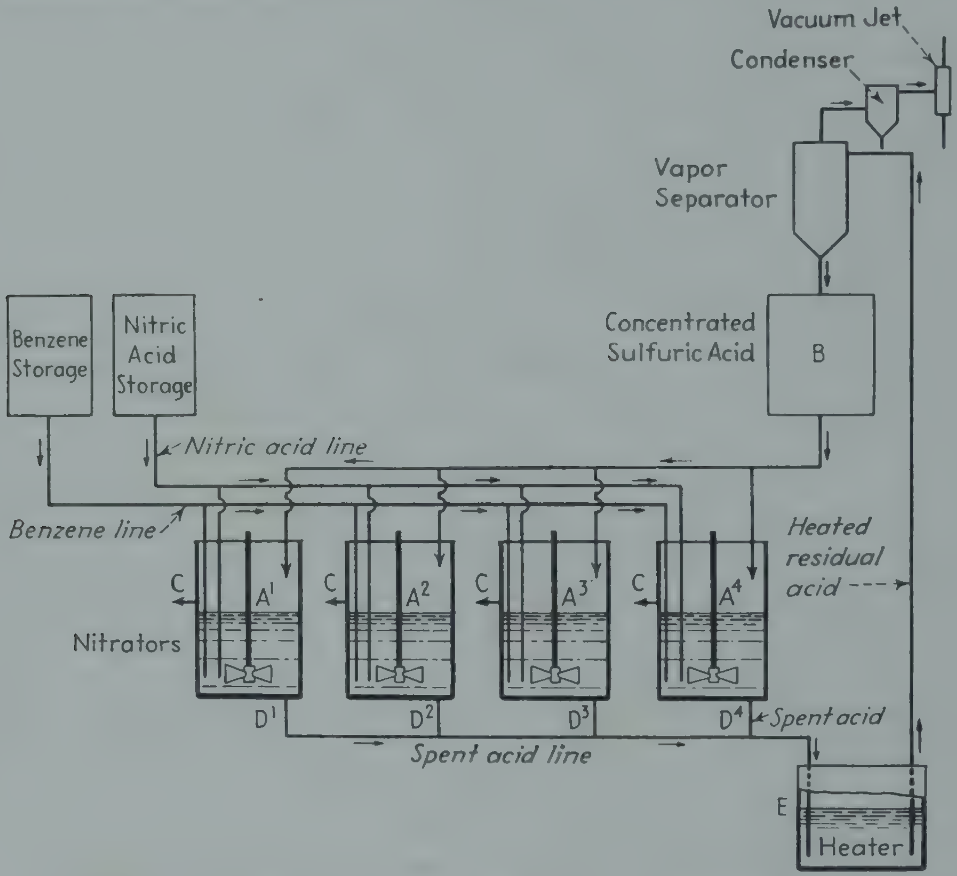
Vacuum Jet
Condenser
Vapor Separator
Benzene Storage
Nitric Acid Storage
Concentrated Sulfuric Acid
B
Nitric acid line
Benzene line
Heated residual acid
C
A¹
A²
A³
A⁴
Nitrators
D¹
D²
D³
D⁴
Spent acid
Spent acid line
E
Heater

FIG. 11.—Nitration of benzene with HNO_3-fortified spent acid.

A^1 to A^4, nitrators.
B. Heat-insulated storage tank for sulfuric acid.
C. Outlets in nitrator for withdrawing nitrobenzene.
D. Outlets from nitrator for drawing off spent acid.

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[1] Castner, U. S. 2,256,999 (1941).

[2] Mares, U. S. 2,370,558 (1945).

As shown in Fig. 11, the operation proceeds as follows: Hot sulfuric acid at 90°C. is run from the heat-insulated storage tank *B* into one of a battery of nitrators A^1 to A^4. Under vigorous agitation, sufficient 63 per cent nitric acid is added to the nitrator to produce a mixed acid containing 4 per cent HNO_3. Sufficient benzene is then delivered from its storage scale tank to react with all the nitric acid in the nitrator. Upon completion of the reaction, which takes about 10 min., the agitation is stopped and the charge permitted to settle. While the separation of the nitrobenzene and spent acid proceeds, another nitration is started, thus providing a continuity of operations.

The crude supernatant nitrobenzene is drawn off through side outlets *C* on the nitrator and sent to the neutralizer. The spent acid, which is free of nitric acid but contains small amounts of nitrobenzene, is drawn off in operating sequence at the outlets D^1 to D^4 located at the base of the nitrators. The spent acid is first directed to the acid heater *E*, which is heated by low-pressure steam to maintain the sensible heat of the spent acid (72 per cent H_2SO_4), and then delivered to the vapor separator. The evaporator, operating under a vacuum of 29 in., effectively removes the water of nitration by virtue of the sensible heat of the spent acid and returns the sulfuric acid to the system at its original (75 per cent) strength. The small quantity of nitrobenzene found with the water in the condenser is separated and added to the crude charge.

The advantages of the preceding nitration process for plants not having acid-concentration facilities are apparent.

Continuous Nitration with Nitric Acid.—Based on findings that nitric acid of about 60 to 65 per cent acidity could successfully be used as a nitrating agent (see Table V) when means were provided for the integrated and continuous removal of water, Othmer's proposal is the plant layout shown in Fig. 12 for the preparation of nitrobenzene.[1]

In this system, nitric acid of approximately 61 per cent strength is delivered continuously from the storage tank *A* to a vaporizer *K* and then introduced into the nitrating column *C* where it comes in contact with descending fresh benzene coming from the storage tank *B* and recovered benzene from the decanter *E*. The reactants then flow to the steam-heated distilling kettle *F* where the nitric acid is dispersed in both the water and benzene phases. The distilling unit is designed to retain a body of reactants and thus permit continued nitration. It is fitted with trays and bubble caps, and the vapor bubbles released on each plate provide considerable agitation and consequently a high rate of reaction. In continuous runs using liquid feed, the conversion of nitric acid to nitrobenzene was approximately 45 per cent of the acid delivered to the system, compared with a yield of 60 per cent when nitric acid vapor was introduced into the nitrating column.

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[1] OTHMER, *Ind. Eng. Chem.*, **34**, 286 (1942).

TABLE V.—VAPOR FEED OF NITRIC ACID

Run No.	40	41	42
Rate of feed, gm./min.	5.83	5.83	1.52
Total acid feed, gm	700.0	706.0	111.0
Time, min	119.0	120.0	120.0
Benzene charged, gm	918.0	992.0	971.0
Temp. of vapors, °C	73	76	72
Temp. of pot, °C	82	82	82
% of acid feed going to pot:			
Water layer	9.8	8.7	7.8
Benzene layer	21.2	18.7	14.0
% of acid feed going to decanter:			
Water layer	6.2	7.3	6.0
To benzene reflux	0.0	1.0	0.2
% of acid feed converted to nitrobenzene	61.0	64.0	63.0
% of benzene charged:			
Going to pot	47.2	46.0	76.8
Going to reflux	14.7	15.2	16.1
Converted to nitrobenzene	35.0	34.0	8.5
% unaccounted for:			
Acid	1.8	0.3	0.9*
Benzene	3.1	4.8	1.4*
Rate of benzene reflux, gm./min	5.0	20.0	5.0
Ratio, benzene reflux/acid feed	0.863	3.44	3.29

* Sum of products greater than sum of reactants due to analytical errors.

The liquid products from the distilling kettle flow into a small distilling column *H* maintained at slightly above 118° to permit separation of the benzene and residual nitric acid from the nitrobenzene (b.p., 208°). The crude nitrobenzene—which may contain traces of benzene—flows out near the base of the distilling column, while the vapors are led to a decanter *G* where the aqueous nitric acid is separated from the benzene-nitrobenzene layer. By means of pump 1, the recovered nitric acid (60 to 68 per cent HNO_3) is returned to the nitrating column.

A constant boiling mixture—consisting of benzene and water—leaves the nitrating column at 72 to 78°. Practically no nitric acid reaches the hot condenser *D* when an adequate reflux is provided in a tall nitrating column. The condensate flows to decanter *E* from which the water of nitration is continuously removed. A means is thus provided for maintaining the nitric acid in the system at the proper nitrating concentration. The recovered benzene leaving the top of the decanter is returned to the nitrating column.

Comparison of Nitrating Procedures. *Materials of Construction.*—In large chemical plants—particularly those making explosives or several

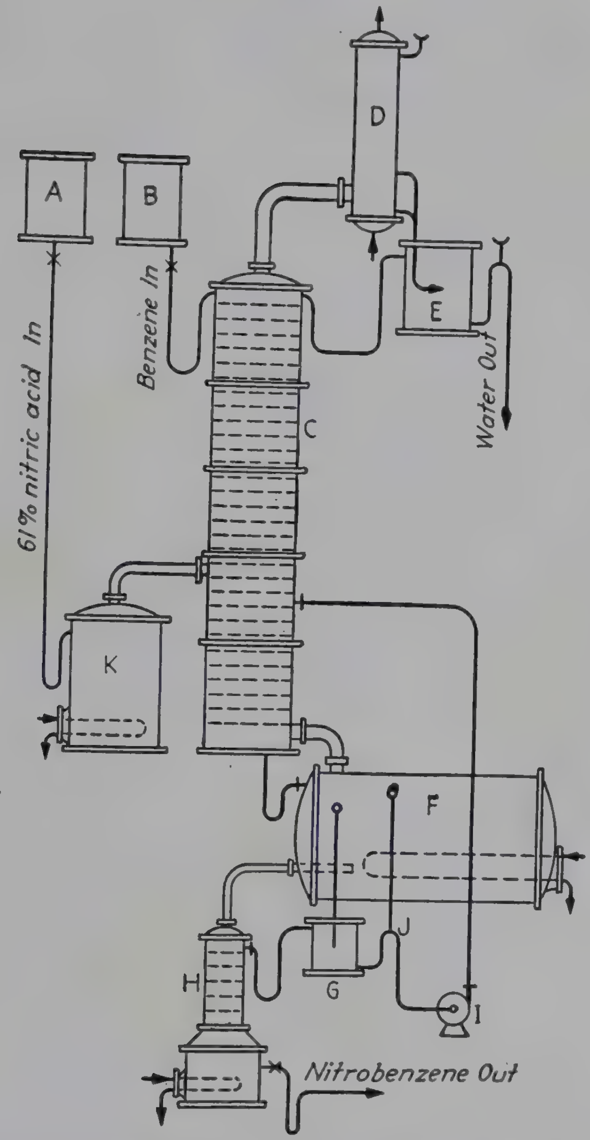


FIG. 12.—Flow diagram for nitration of benzene with nitric acid.

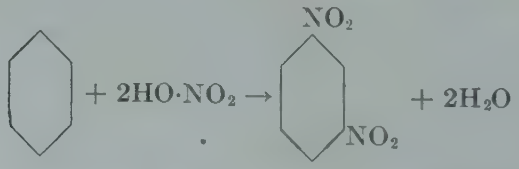
A. Nitric acid storage (61 per cent HNO_3).
B. Benzene storage.
C. Nitrating column (approximately 30 in. in diameter).
D. Hot condenser.
E. Decanter for separating hot benzene and water condensate.
F. Distilling kettle with heating coils for steam.
G. Decanter for separating the nitric acid and benzene-nitrobenzene layers leaving the distilling kettle.
H. Distilling column for separating benzene and dissolved nitric acid from nitrobenzene, equipped with base heater.
I. Pump for recycling nitric acid and water layer back to nitrating column.
J. Vent line to distilling kettle.
K. Nitric acid vaporizer.

nitro compounds—the concentration of spent acid derived from the use of mixed acids is economically carried out in a central plant. When mixed acid or HNO_3-fortified spent acid is employed in isolated operations, the water of nitration must be removed from the system H_2SO_4-H_2O, thus permitting the use of equipment involving inexpensive materials of construction. When nitric acid is used as the nitrating acid, a suitable chrome-nickel steel alloy must be used throughout, because every part of the system is exposed to liquid or vaporous nitric acid.

Operating Efficiency.—When mixed acid is used as the nitrating agent, approximately combining proportions of the reactants are used. Although the use of HNO_3-fortified spent acid entails handling a larger volume of sulfuric acid, the water of nitration per pound of nitrobenzene is the same. In both instances, there is complete or practically complete utilization of the hydrocarbon as well as the HNO_3 in the nitrating acid. When nitric acid is employed, a large excess of benzene must be maintained in the nitrator, and complete utilization of reactants depends on evaporation, condensation, and recycling. In any event, it is doubtful if any one of the three processes has an appreciable advantage with respect to operating efficiency.

Heat Consumption.—In the absence of detailed information, it may be presumed that the use of HNO_3-fortified cycle acid, where water is removed from hot, spent acid under reduced pressure, constitutes the most economical system insofar as heat input is concerned, notwithstanding the fact that sulfuric acid has a greater heat of hydration than nitric acid. Where opportunities are afforded for the advantageous concentration or outside disposal of spent acid to manufacturers of superphosphate fertilizers, the use of mixed acid in a battery of nitrators permits operations in a compact and comparatively inexpensive plant.

PREPARATION OF *m*-DINITROBENZENE



The preparation of *m*-dinitrobenzene from benzene is usually accomplished in two stages of nitration. Both may, however, be made to take place in the same vessel.

The first stage is carried out under the conditions previously described for nitrobenzene. At the conclusion of the first nitration, the spent acid is run off from the base of the machine and is replaced by a stronger nitrating acid for the second stage of nitration. The composition of the nitrating acids for the two stages of nitration is as follows:

MIXED ACID COMPOSITIONS

(I) For Mononitration %		(II) For Dinitration %
60.0	H_2SO_4	75
32.0	HNO_3	20
8.0	H_2O	5
3.52	D.V.S.	7.36
1.01	HNO_3 ratio	1.1

It is readily seen from the above acid compositions that the second nitration requires a more concentrated acid. Moreover, the reaction must be controlled at a higher temperature, *i.e.*, 100 to 110°C. Although the heat of nitration for the second nitro group is not so great as for the introduction of the first, the operation is nevertheless much slower on account of the lower specific heat and greater integral heat of dilution of the more concentrated acids that are used.[1] Since the rate of feed and time of reaction are determined by the efficiency of agitation and heat exchange, these are therefore matters of special importance in this nitration.

Stirring is continued after the acid is all in and until the nitration is finished, this being indicated by the solidification, upon cooling, of the oily portion of a sample withdrawn from the machine. By stopping the agitation and maintaining the temperature at approximately 100°C., the contents of the nitrator are made to separate in two layers—an upper, lighter, aromatic nitro compound and a lower, spent acid. After drawing off the spent acid, the dinitrobenzene is run into a vat containing boiling water, which is thoroughly agitated, preferably by live steam admitted through a circular spider. The washing is repeated with the addition of alkali, as in the preparation of nitrobenzene, to ensure an acid-free product. A final treatment with boiling water completes the preparation of the crude product. The dinitrobenzene obtained in this way melts at 78 to 80°C. and contains about 8 per cent ortho and para isomers. The spent acid from the dinitration (approximately 85 per cent H_2SO_4) contains from 8 to 10 per cent nitro compound in solution (see solubility curves, Fig. 6), and this must therefore be diluted to precipitate the dissolved dinitrobenzene.

Hough has suggested the preparation of *m*-dinitrobenzene directly from benzene.[2] By using a mixed acid A′ (Fig. 13), the highest yield

Mixed acid A′	H_2SO_4	80.0
	HNO_3	18.0
	H_2O	2.0
	D.V.S.	11.96
	HNO_3 ratio	1.1

of the meta compound is obtained, the product having a melting point of 83°C. Mixed acid A″ gives a product setting at 79°C.; and A‴, 75°C. The temperature must be held at 30°C. while the benzene is being added to the cycle acid and then permitted to rise gradually to 100°C. during the time for completion of the reaction. The spent acid from A′ will be B′, which is located below the perfect nitration line due to the reduction of a small part of the nitric acid and the formation of nitrosylsulfuric acid.

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[1] Rhodes and Nelson, *Ind. Eng. Chem.*, **30**, 648 (1938).

[2] Hough, *Chem. Met. Eng.*, **23**, 668 (1920).

The only method known for recovering B′ spent acid is to dilute to C′, practically all of the nitrosylsulfuric acid being decomposed and 7 of the 8 per cent dinitrobenzene dissolved in the acid being liberated by the operation. After denitration, the last traces of organic matter are removed by concentrating the sulfuric acid to a strength of 96 per cent.

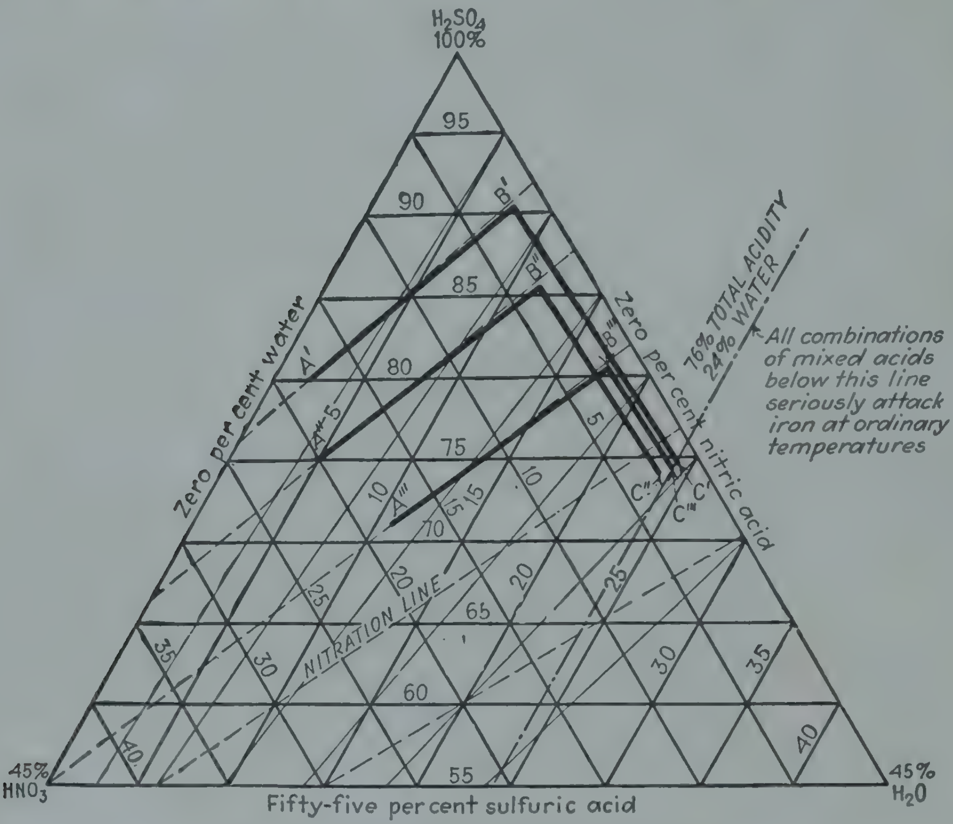


FIG. 13.—Mixed acid system for nitrations.

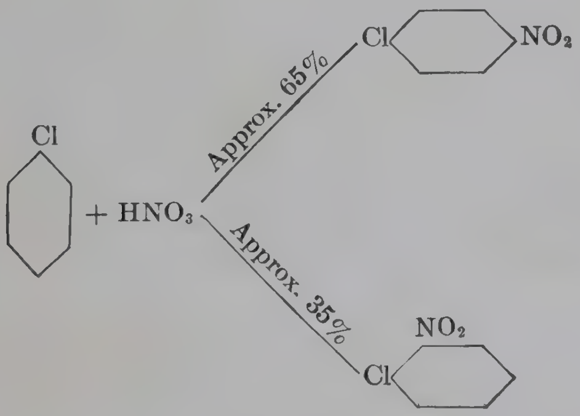
Figure 13 is a three-coordinate chart having sulfuric and nitric acids and water percentages as variables. A percentage of any one of the constituents is represented by a line. A dot-and-dash line represents 24 per cent water, which is the limit of dilution permissible for nitration in iron vessels. Above this, practically no hydrogen ions are present at the nitrating temperatures, and a mixed or spent acid with less than 24 per cent water does not appreciably attack steel. The percentages of any two constituents fix the third and locate a point, A″ for instance being 5 per cent water, 75 per cent sulfuric, and 20 per cent nitric acid. The dotted fine lines are the loci of molecular substitution of nitric acid by water and represent the sulfuric-water concentration throughout the mixed acid medium.

The purification of *m*-dinitrobenzene may be effected by making a paste with the least possible quantity of warm benzene or toluene and then filtering the cooled mass. Another method of purification is based on the greater instability of the ortho and para isomers in dilute caustic. When crude *m*-dinitrobenzene containing 6 to 10 per cent impurities in the form of isomers is treated with a 5 to 10 per cent caustic solution at a temperature above the melting point of the product (90 to 100°C.), the ortho and para isomers that are converted to the corresponding nitrophenols are removed as soluble alkali salts with the alkaline solution. The *o*-nitrophenol present in the largest amount in the alkaline wash waters may be recovered by acidifying and distilling with steam. This method of purification has been used extensively in the separation of isomeric compounds, *e.g.*, the removal of *o*- from *p*-nitroaniline. When basic substances are being purified, acids are used as solvents. Under such circumstances, the meta compounds, which are usually the strongest bases, dissociate most and remain in solution, whereas the ortho and para compounds are separated by precipitation.

Purification may also be effected by suspending 100 parts of the crude product in 200 parts of water at 85 to 90°C. and then rapidly cooling to 45°C. to obtain a fine crystalline dispersion of dinitrobenzenes. To this suspension, 15 parts sodium sulfite and 20 parts sodium bisulfite are added, and the charge is stirred for about 2 hr. at a temperature of 60°C. Upon cooling to 30°C. and then filtering and washing, *m*-dinitrobenzene (m.p., 90.6°C.) is obtained in a yield of 84 per cent.[1]

PREPARATION OF *o*- AND *p*-CHLORONITROBENZENE

The preparation of chloronitrobenzene is of interest because of its commercial preparation by nitrating chlorobenzene with an alkali nitrate and sulfuric acid.



In carrying out the process, a mixture of 1,000 lb. sulfuric acid, 81 per cent strength, and 200 lb. chlorobenzene is heated to 100°C. in a jacketed nitrator equipped with an effective stirrer. To the hot agitated emulsion, which is controlled by the use of steam or water in the jacket, at 110 to 130°C., are added 1,175 lb. of dried, pulverized, commercial sodium nitrate and about 1,600 lb. of 93 per cent sulfuric acid. Concurrently 1,240 parts of chlorobenzene are added at such a rate that proportional parts of the reactants are admitted in about the same period of time. Under such conditions, nascent HNO_3 is progressively generated; and with optimal conditions, not more than small amounts of unreacted sodium nitrate are present in the charge. The heat of nitration raises the temperature above 110°C.; and at first the use of cooling water is neces-

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[1] U. S. 2,040,123 (1936).

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sary to limit the temperature to a maximum of 130°C. The addition of the reacting materials requires about 5 hr., after which the temperature is maintained by the existing heat-exchange facilities at 110 to 130°C. for 1 hr.

The contents of the nitrator are permitted to settle, and the waste acid and dissolved sulfate are drawn off from the bottom. The oily mixture of isomeric chloronitrobenzenes is then delivered to a vat in which it is washed with hot water and hot dilute alkali.

Some of the calculations pertaining to the above nitration are as follows:

$$\frac{\text{(Chlorobenzene)}\ 112.5}{(\mathrm{HNO_3})\qquad 63} : \frac{1440}{X} \quad X = 806 = \text{lb. } \mathrm{HNO_3} \text{ required for}$$

1,440 lb. charge chlorobenzene.

1,175 lb. $NaNO_3$ × 96% purity × .741 (HNO_3 factor) = 836 lb. HNO_3 available.

$$\text{The ratio } \mathrm{HNO_3} \text{ to chlorobenzene } \frac{836}{806} = 1.037$$

The D.V.S. of the nitrating acid may be calculated from the acid components used.

1,000 lb. H_2SO_4 at 81%	= 810	65.4% H_2SO_4
1,600 lb. H_2SO_4 at 93%	= 1,448	
Estimated 850 lb. HNO_3	= 837	24.3% HNO_3
H_2O by difference	356	10.3% H_2O
3,450 lb.	3,450	100.0%

Water of nitration per 100 lb. $M/A = 6.72$ (103.7 acid ratio)

$$\text{D.V.S.} = \frac{65.4}{6.7 + 10.3} = 3.85$$

The above acid mixture is, as has been previously observed, satisfactory for carrying out mononitrations.

By the substitution of nitrate and H_2SO_4 for mixed acid, it appears that a great economy has been effected, because it would have required about 1,200 lb. of sulfuric acid to produce the necessary amount of nitric acid from sodium nitrate for the above operation. Furthermore, the yields in nitric acid operations are usually about 98 per cent of theory, whereas no appreciable losses are sustained in this procedure. On the other hand, the nitration waste from this operation is a mixture of dilute sulfuric acid and impure sodium acid sulfate as compared with a completely recoverable sulfuric acid from mixed acid nitrations. A further disadvantage arises from the fact that nitration with nitrates requires a slightly greater excess of HNO_3, which is not susceptible to economical recovery.

When the nitration of chlorobenzene is made with mixed acid, Hough recommends an acid of the following composition:[1]

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[1] Hough, *Chem. Met. Eng.*, **23**, 668 (1920).

$$\begin{aligned} H_2SO_4 &= 71.0\% \\ HNO_3 &= 18.0\% \\ H_2O &= 11.0\% \\ \text{D.V.S.} &= 4.41 \\ HNO_3 \text{ ratio} &= 1.01 \end{aligned}$$

The D.V.S. in this acid is close to that used in making the nitration of benzene; and, when only a slight excess over the required amount of nitric is used, the yield of nitroaromatic compound is practically theoretical.

The separation of the nitrochlorobenzenes (about 35 per cent ortho and 65 per cent para) is a tedious and difficult matter. The solidifying points of mixtures of *o*- and *p*-nitrochlorobenzenes are given in Table VI. From this table, it is seen that the eutectic point is 14.65°C., corresponding to a composition of 33.1 per cent of para and 66.9 per cent of ortho compound.

Table VI.—Solidifying Points, Mixtures, *o*- and *p*-Nitrochlorobenzenes[1]

Para, %	Solidifying point, °C.	Para, %	Solidifying point, °C.
0	32.09	34.09	16.73
6.54	29.00	35.43	18.43
12.61	26.10	41.67	28.50
19.22	22.65	48.94	37.65
26.89	18.30	68.54	57.83
32.39	15.35	75.48	63.97
32.90	14.85	90.30	75.40
33.07	14.77	95.57	79.13
33.10	14.65	100.00	82.15

[1] According to Holleman, *Proc. Acad. Sci. Amsterdam*, **11,** 248 (1908).

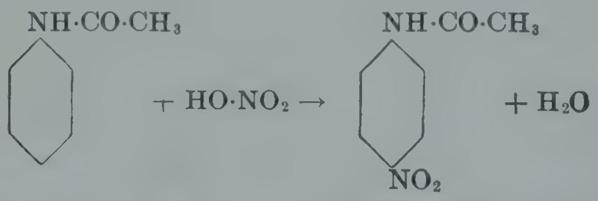
The separation of the isomers may be accomplished by alternate crystallizations and distillations, taking advantage of the slight differences in their physical constants. From the melting and boiling points of the two compounds given below, along with the information derived from the melting points of the mixtures, it can be predicted that considerable of the para content will be thrown out upon cooling. Half of the para compound is recovered in this way by first cooling the nitration product

	Melting point, °C.	Boiling point, °C.	
		760 mm.	8 mm.
Ortho	32.5	245.7	119
Para	83.5	242.0	113

to 16°C., *i.e.*, a little above the eutectic point. The filtrate is then distilled *in vacuo*. The product first coming over is chlorobenzene. The second fraction is essentially the para, and that coming over last is essentially the ortho compound. If these fractions are cooled, the isomers may be separated and purified by washing with methanol.

The separation of the isomers may also be effected by dinitrating the oily eutectic fractions at 60 to 100°C., whereby the ortho isomer reacts preferentially and is to a large extent converted to 2, 4-dinitrochlorobenzene.[1] An excellent separation of the isomers can be obtained by distilling *in vacuo*, using a tall column filled with rings and maintaining a vapor velocity of 0.5 m. per sec. (see Separation of Nitrotoluenes, page 56). According to this procedure, practically pure compounds are obtained, except in separating part of the para fraction when a liquid mixture containing 35 per cent of *p*-nitrochlorobenzene remains. This mixture is incorporated with fresh material to be rectified.

PREPARATION OF *p*-NITROACETANILIDE



In the nitration of acetanilide, it is important, in order to prevent hydrolysis, to conduct the nitration at 3 to 5°C. To ensure a maximum yield of product, use is made of cycle acid, which in this instance is water-white 66°Bé. sulfuric acid. Into 4,000 lb. of sulfuric acid that is free of nitrous acid is delivered very slowly 1,000 lb. of dry acetanilide (m.p., 113°C.). During the 3 to 4 hr. that are consumed in this operation, the temperature is maintained at 25°C. The charge is cooled to 2°C., and 1,450 lb. of mixed acid of the following composition is then slowly run into the nitrator, the rate of feed being regulated by the capacity of the brine coils to control the temperature at 3 to 5°C.

Composition of nitrating acid	HNO_3	33 %
	H_2SO_4	47 %
	H_2O	20 %
	HNO_3 ratio	1.015

Agitation is continued for 1 hr. longer, the entire operation consuming from 10 to 12 hr. When the temperature rises above 5°C. during nitration, there is a distinct tendency toward the formation of the ortho isomeride. To test for complete nitration, a sample is drawn from the nitrator and poured on ice, and the *p*-nitroacetanilide washed with cold water. The precipitate is hydrolyzed in a test tube with boiling dilute caustic, and the resulting *p*-nitroaniline should yield a clear yellow solution with hydrochloric acid. If the acetanilide has not been completely nitrated, the odor of aniline may be detected.

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[1] U. S. 1,981,311 (1934).

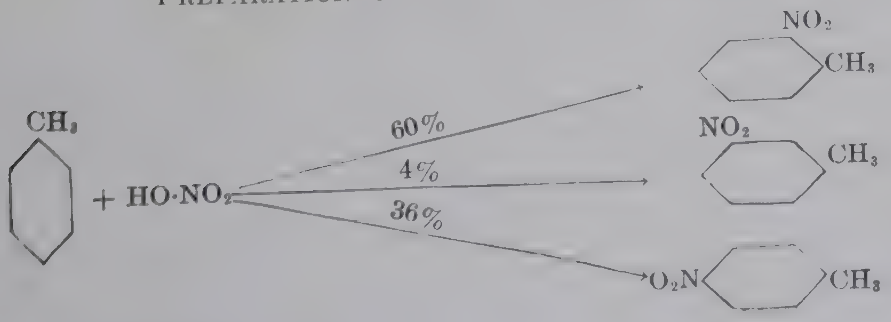
The batch is run from the nitrator on to a suction filter containing 600 gal. of water and sufficient ice (or a brine coil) to keep the temperature below 15°C. The filter is a large wooden tub 8 ft. in diameter having a false bottom of filtros tile. It is provided with a stirrer that is set in motion just prior to receiving the charge from the nitrator. The temperature should be kept close to 5°C.; otherwise, the weak mineral acid present will hydrolyze some of the *p*-nitroacetanilide and the mixture will turn yellow owing to the formation of *p*-nitroaniline sulphate. Part of the amino compound will consequently be lost during the ensuing filtering and washing operations, and a low yield will be the result. The *p*-nitroacetanilide, which is brown as it runs from the nitrator, is changed to a milky-white mass as it comes into contact with the cold water.

When the *p*-nitroacetanilide is to be sold, it is twice washed on the filter with cold water until practically free of acid and then with a minimum of 3 per cent caustic soda or sodium carbonate solution. The neutralized cake is finally washed to remove the excess of alkali and then removed and dried. For the production of *p*-nitroaniline, the filter cake is merely washed and delivered to the hydrolyzing kettle.

Any *o*-nitroaniline can be separated on the filter by making the batch slightly alkaline with 20 to 30 lb. of 3.5 per cent sodium hydroxide and heating the charge containing a minimum amount of water up to 80°C. The alkaline liquor containing the soluble salt of the enolized ortho isomeride can then be filtered off. The ortho compound may similarly be removed by continued washing with hot water at 80°C. Separation of the ortho isomeride may also be effected by diluting the nitrator charge with cold water so as to obtain a sulfuric acid concentration of 65 per cent. The suspension is then warmed to 70°C., whereby hydrolysis of the acetyl group is effected. Upon cooling to 0°C., the *p*-nitroaniline sulfate separates out and is recovered by filtration.[1]

The yield of *p*-nitroacetanilide is 88 to 90 per cent of theory, or 160 to 162 lb. per 100 lb. acetanilide taken.

Preparation of Mononitrotoluenes



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[1] Flett, U. S. 2,012,307 (1935).

The nitration of toluene is carried out in a manner similar to that used in the preparation of nitrobenzene and the chloronitrobenzenes. The presence of the methyl group may, however, give rise to the formation of oxidation impurities if the temperature is excessive. Thus, whereas a temperature in excess of 100°C. may be used for the nitration of chlorobenzene, that during the mononitration of toluene is controlled between 30 to 60°C. The ease of oxidation increases as methyl groups are added to the ring. It is necessary, therefore, to moderate progressively the nitrating conditions in the series toluene, xylene, and cumene.

Toluene is first run into the nitrator containing cycle acid, and the mixture is cooled to approximately 30°C. Mixed acid is added slowly to the well-stirred charge, controlling the temperature at 50°C. The agitation is continued under these conditions for 2 hr. after the acid is all delivered.

The nitrating acid need not be quite so concentrated as that used in the preparation of nitrobenzene, and a fortified spent acid can be used advantageously; for in this case, the reaction takes place more readily. The composition of typical mixed acids, according to Holleman (I) and Gibson (II), are as follows:[1,2]

I		II
57.6%	H_2SO_4	58.7%
30.0%	HNO_3	23.8%
12.4%	H_2O	17.5%
2.84%	D.V.S.	2.42%
1.09	HNO_3 ratio	1.01

The yield of mixed nitrotoluenes is about 96 per cent of theory. The relative proportion of each isomer is approximately 60 per cent ortho, 4 per cent meta, and 36 per cent para. These proportions are practically constant and do not appear to be affected sufficiently by variations in the process to make the suppression of *m*-nitrotoluene feasible.

The separation of the mixed nitrotoluenes may be carried out in a manner similar to that used for the isomeric chloronitrobenzenes. When

Isomeride	Melting point, °C.	Boiling point, °C.
Ortho, α[1].	−10.56	222.3
Ortho, β.	− 4.14	222.3
Meta.	16.10	230.3
Para.	51.60	238.0

See Bell and collaborators[1] for discussion of two forms of *o*-nitrotoluene.

[1] BELL, GORDON, SPRY, and WHITE, *Ind. Eng. Chem.*, **13**, 59 (1921).

[1] HOLLEMAN, *Proc. Acad. Sci. Amsterdam*, **11**, 248 (1908).

[2] GIBSON, DUCKHAM, and FAIRBAIRN, *J. Chem. Soc.*, **121**, 270 (1922).

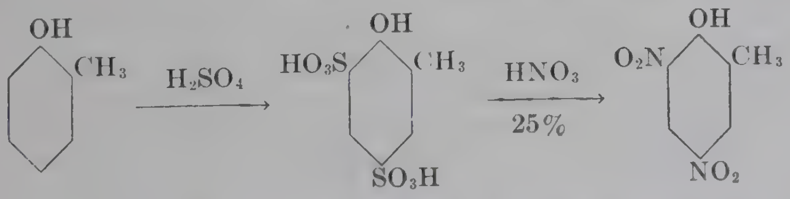
the nitration product is distilled *in vacuo*, the first fraction is essentially the ortho compound. When cooled to 10°C., this liquid fraction deposits any accompanying para compound. After the distillation has gone halfway, the contents of the still are cooled and crystallized, and the para compound may thus be separated by centrifuging. The middle fraction is added to new material and redistilled.

Separations of the isomeric nitrotoluenes can satisfactorily be effected in a tall column filled with Raschig rings. Distillation under 20-mm. pressure and control of the dephlegmator at constant temperatures by automatic increase or decrease of heat-exchange fluid afford excellent results. When this method is applied to the separation of *o*- and *p*-nitrotoluenes, a 45 per cent yield—based on the total charge—of technical ortho compound is obtained by such a procedure. The para isomeride is then recovered by cooling the residue with brine or by continuing the rectification and separating the intermediate fraction from which more para compound may be recovered on cooling.

The Preparation of Dinitrocresols

The preparation of *o*- and *p*-nitrophenol is usually accomplished by treating the corresponding chloronitrobenzene derivatives with dilute alkali. This procedure, which is productive of practically theoretical yields of the desired product, is described under Hydrolysis.

Procedures for the dinitration of *o*- and *p*-cresols have been reported by Filbert and by Dolt and Hill.[1,2] The processes, which are similar, involve the treatment of the cresol with sulfuric acid at sulfonation temperatures, followed by reaction with dilute nitric acid. This method is also employed in the preparation of picric acid from phenol where it has been found desirable to make phenoldisulfonic acid first.



One hundred pounds of sulfuric acid of 93 per cent strength is added gradually to 50 lb. of liquid *o*-cresol, which is vigorously stirred and the sulfonation continued for 15 min. after reactants are introduced. There is no cooling of the reaction mixture, the temperature being permitted to rise at will.

The charge from the sulfonator is then added gradually to a vigorously stirred mixture containing 186 lb. of water and 135 lb. of 60 per

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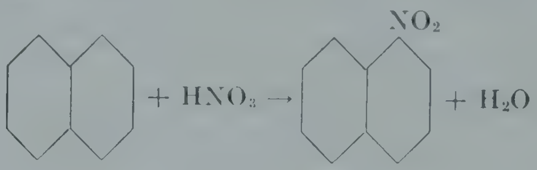
[1] Filbert, U. S. 2,256,195 (1941).

[2] Dolt and Hill, U.S. 2,325,753 (1943).

cent nitric acid, which is maintained by external cooling at 74°C. Fifty-five minutes are required for this addition, following which nitration is allowed to proceed for an additional 10 min. The charge is then cooled to 49°C., and the crude 4, 6-dinitro-*o*-cresol filtered off. The material on the filter is given several cold-water washes and is then introduced into a vessel containing 100 lb. of water heated to about 92°C. which is stirred actively. Upon addition, the dinitro-*o*-cresol becomes molten almost immediately and is dispersed throughout the water. Sufficient cold water is then added to cool the suspension to 74°C., the rate of addition of water being such that the dinitro-*o*-cresol is suitably grained. The temperature is then decreased further, solely by external cooling to about 48°C., and the charge is then filtered and washed with cold water. A 77 per cent yield of 4, 6-dinitro-*o*-cresol is obtained as a bright yellow granular product, having a melting point of 84.4°C.

In a similar manner, *p*-cresol can be dinitrated and a product melting at 79 to 81 ° is obtained.

Preparation of α-Nitronaphthalene



When naphthalene is nitrated under optimal conditions, the product consists principally of α-nitronaphthalene. The reaction takes place vigorously; and unless precautions are taken, polynitro compounds are formed. If impure naphthalene is used, the nitration product will be unsatisfactory; and inasmuch as it is difficult to isolate α-nitronaphthalene in a pure state, it is advisable to prevent further complications and to use a pure raw material.

When the nitration is made without the use of cycle acid, a mixed acid of the following composition may be used:

H_2SO_4	59.55%	HNO_3 ratio	1.01%
HNO_3	15.85%	D.V.S.	2.04%
H_2O	24.60%		

This will yield a product consisting of 95 per cent α-nitronaphthalene together with some unchanged naphthalene and very little dinitro derivative.

By using cycle acid to dissolve the naphthalene to be nitrated and then proceeding with the nitration in the usual way, the operating steps are as follows: The naphthalene—1,280 lb.—is suspended in 4,500 lb. of dilute sulfuric acid or spent acid containing about 65 per cent H_2SO_4.

The whole is thoroughly stirred, and 2,350 lb. of mixed acid of the following composition is slowly added:

H_2SO_4	56.60%
HNO_3	28.30%
H_2O	15.10%
HNO_3 ratio	1.03%

During the addition of the acid, the temperature is kept at 25 to 30°C.; but after the whole of the acid has been run in, the temperature is raised slowly to 65 to 70°C. and maintained at that point for 1 hr. The agitation is then stopped, and the nitronaphthalene which floats on the surface as a porous cake is separated from the spent acid in a separator.

The crude product is delivered to the neutralizing kettle, where it is made free of acid by repeated washings with boiling water and alkali. Any free naphthalene that may be present is removed by steam during the washing process.

The purification of the crude product is accomplished by recrystallizing it from 10 per cent of its weight of ligroin or solvent naphtha. The success of the purification depends upon certain details of manipulation, which include (1) use of a minimum of solvent and (2) constant agitation while recrystallization takes place in order to assure the formation of small crystals. The nitronaphthalene is dissolved in 10 per cent of its weight of solvent naphtha and heated above the melting point of the crude, *i.e.*, above 50°C., until a homogeneous mixture is formed. The resulting solution is cooled to 25°C. with constant agitation, and the thick slurry that is formed is centrifuged. The α-nitronaphthalene obtained in this manner has a solidifying point above 54.4°C. This is not yet pure, as the c.p. material comes as glistening yellow crystals which melt at 61°C. To obtain the pure product, it is necessary to resort to further purification by recrystallization.

THE PREPARATION OF NITROPARAFFINS[1,2]

The liquid-phase nitration of paraffinic hydrocarbons is confronted with certain inherent difficulties. Nitric acid and the alkanes are mutually insoluble, whereas the nitrated product is considerably more soluble in the nitric acid layer and is there subjected to further nitration, hydrolysis, and oxidation. These particular difficulties may be obviated by operating in the vapor phase. The reactants may then be mixed in any desired proportions; and, inasmuch as reaction is almost instantaneous, practically no polynitro derivatives are formed. Operations

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[1] HASS, HODGE, and VANDERBILT, *Ind. Eng. Chem.*, **28**, 339 (1936); U. S. 1,967,667 (1934); 2,071,122 (1937).

[2] MCCLEARY with DEGERING, *Ind. Eng. Chem.*, **30**, 64 (1938).

according to this method are particularly suitable for the lower paraffins, and such nitrations may be carried out in the apparatus shown diagrammatically in Fig. 14.

The alkane, at atmospheric or superatmospheric pressure and in the vapor phase, is delivered to a mixing tube where it is intimately mixed with an atomized stream of nitric acid delivered under pressure. To increase the yield of nitroparaffins and to decrease explosion hazards, it is important to regulate the proportions of the reactants so as to have at least 2 moles of alkane per mole of nitric acid. The mixture of hydrocarbon and acid vapors passes through a chrome-nickel steel alloy or fused silica reaction tube, immersed in a suitable salt bath maintained at 410 to 480°C. When a ferrous material such as stainless steel is used as a reactor, it is desirable to impinge the incoming gaseous paraffins on the surface of a molten nitrate salt[1] and entrain small quantities of such materials as reactivation agents or to pass the vaporized reactants through a heated catalyst chamber packed with fragments of borosilicate glass containing compounds of arsenic and antimony[2] in order to overcome the tendency to lower conversions of nitric acid to nitroparaffins caused by the deposition of metallic oxides on the reactor surfaces.

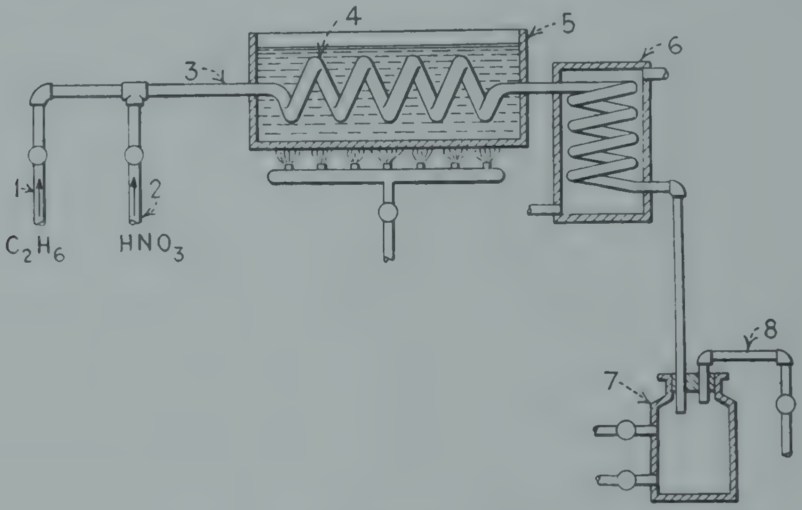

FIG. 14.—Reaction system: vapor-phase nitration of paraffins.

1. Metered inlet for alkanes.
2. Inlet for nitric acid vapors.
3. Mixing tube.
4. Reaction coil.
5. Furnace containing molten salt.
6. Cooling coil.
7. Liquid-gas separator.
8. Vent for uncondensed gases.

Hodge has found that in the nitration of alkanes the reaction temperature or contact time or both should be increased or decreased when the acidity of the reaction products rises above or falls below certain desired levels—0.3 *N* to 0.5 *N*. Thus if the acidity of the aqueous layer rises above the optimum range, the reaction temperature should be increased and/or the contact time increased (space velocity decreased) thus to effect greater utilization of the nitrating agent. When automatic control of the acidity is maintained, more uniform and more efficient operations are possible.

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[1] Martin, U. S. 2,260,258 (1941).

[2] U. S. 2,394,315 (1946).

The mixed gases from the reaction tube contain nitroparaffins, water vapor, unreacted nitric acid, oxides of nitrogen, unreacted paraffin hydrocarbons, and small amounts (4 gm. per 100 cu. ft. of exit gases) of aldehydes and ketones. These gases are first directed through a cooler maintained at a temperature that will ensure condensation of the nitroparaffin at atmospheric pressure. The condensed liquid and accompanying gases pass to a liquid-gas separator in which the liquid nitro compounds and spent acid are collected. The liquid product separates into two layers, and the supernatant mixture of nitroparaffins is drawn off and subsequently purified by washing thoroughly with water and then rectifying in a Podbielniak or other suitable column. The lower oxides of nitrogen are oxidized and reemployed.

The carbonyl compounds that accompany the unreacted alkanes leaving the liquid-gas separator adversely affect the conversions if they are permitted to remain with the separated paraffins in a recycling process. Ordinary washing or washing with alkaline solutions does not satisfactorily effect their removal. Martin and Hodge have proposed supplementary scrubbing of reaction gases with 70 per cent sulfuric acid[1] followed by reduction by hydrogen in the presence of a nickel catalyst[2] as removal procedures. The purified alkane is then recovered and recycled.

TABLE VII.—NITRATION OF PARAFFINS; RESULTS OF ANALYSES, %

Hydrocarbon	Acetone	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	1-Nitroisobutane	2-Nitroisobutane	Yield per pass
Methane	. .	. . . . .	. . . . .	. .	. .	. .	. .	. .	. .	0
Ethane	. .	10–20	80–90	. .	. .	. .	. .	. .	. .	9
Propane	. .	9	(26?)	32	33	. .	. .	. .	. .	21
Butane	. .	6	12	5	. .	27	50	. .	. .	28
Isobutane	5	3	. . . . .	. .	20	. .	. .	65	7	25

According to Hass, Hodge, and Vanderbilt.

The results of nitrations carried out substantially as noted above gave the results set forth in Table VII.

In general, it is found that the use of superatmospheric pressures in the reactor leads to an increase in the yield of nitroparaffins and a large increase in the reaction rate. The yield is also increased by increasing the ratio of hydrocarbon to nitric acid in the reacting gases up to a ratio of 14.1.

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[1] Martin and Hodge, U. S. Reissue 21,657 (1941).

[2] Hodge, U. S. Reissue 21,658 (1940).

The introduction of oxygen-containing gases favors oxidation with no increase in nitration. This is probably due to the fact that the equilibrium

$$2NO_2 \rightleftharpoons 2NO + O_2$$

is displaced completely to the right, above 154°C.; and, as is well known, the lower oxides of nitrogen are the more vigorous oxidizing agents.

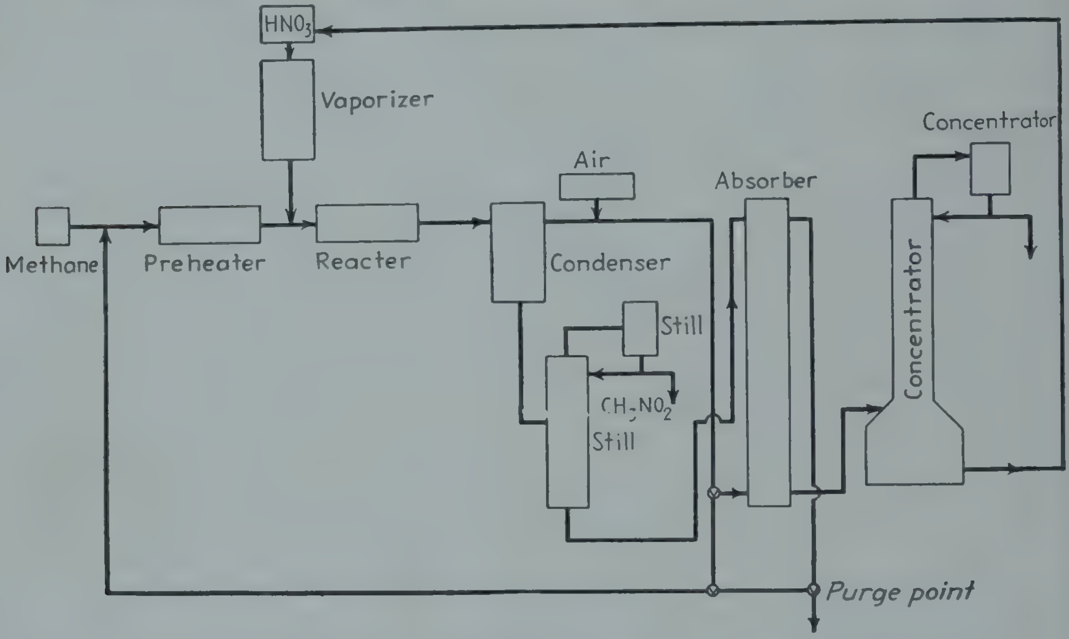

FIG. 15.—Flow diagram: nitration of methane.

The Nitration of Methane.—In the nitration of paraffins, the production of nitromethane has presented acute problems due to low conversions and difficulty in recovering the unreacted methane to permit its recycling to the nitrator. Rideout has shown that these problems can, to a large extent, be obviated by using a single-pass nitration wherein the methane is diluted by a recirculated inert gas such as nitrogen. When the methane content of the gas mixture is reduced to about 10 to 15 per cent, relatively high yields of nitromethane are obtained. The following data show the improvement in yields of nitromethane occasioned by dilution of reactants with nitrogen.[1]

% methane in gas entering reactor;	10	25	35	50	75	100
% CH_4 converted to nitromethane;	6.4	5.1	4.7	3.7	3.1	2.2

As shown in Fig. 15, the operations can be carried out in a continuous manner as follows: Methane admixed with recirculated gases is led through a preheater and then mixed with nitric acid vapors. The combined gases enter a reactor which is maintained at about 470°C. and 100 lb. pressure. A contact time of 0.30 sec. is allowed, and the reaction gases comprising nitromethane, nitrogen oxide, and carbon oxides are led to a condenser, where the nitromethane and nitric acid are liquefied. The more volatile nitromethane is separated from the acid liquor in a still, the residual nitric acid being removed at the base and circulated over the absorber. The dilute acid formed in the absorber is concentrated to 40 per cent strength for reuse.

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[1] Rideout, U. S. 2,291,345 (1942).

The effluent gases from the condenser are mixed with air which furnishes the oxygen to convert the nitrogen oxide to nitric acid. The absorption and oxidation of nitrogen oxide in the presence of water takes place in the absorber. The excess of uncondensed gases leaving the absorber are purged, and the balance is recirculated to the junction point where it meets fresh methane.

Effect of Temperatures.—The effect of increased temperature upon the vapor-phase nitration reaction is to increase (1) its velocity, (2) the yield of fission products, and (3) the production of primary nitroparaffins at the expense of secondary and tertiary isomers. This change in ratio is probably due primarily to a change of the relative reaction rates of the primary and secondary hydrogen atoms with the change in temperature. The results obtained in the nitration of butane are presented in Table VIII.[1]

TABLE VIII.—EFFECT OF TEMPERATURE: NITRATION OF BUTANE

Run No.	Temp., °C.	Nitromethane, %	Nitroethane, %	1-Nitropropane, %	2-Nitrobutane, %	1-Nitrobutane, %
1	395	2.1	12.7	4.9	49.0	30.5
2	393	6.0	19.0	7.0	41.0	27.0
3	393	5.0	11.0	5.0	46.0	32.0
4	445	5.9	18.2	6.5	37.0	31.8
5	450	9.0	25.0	7.0	28.0	31.0

Material Cost of Production of Nitroparaffins.—Yields of 40 per cent per pass have been obtained in the nitration of the butanes. Since not more than 5 per cent of the nitric acid is reduced to free nitrogen, this means a net, over-all yield of (40 × 100)/(40 + 5) or 89 per cent, based upon nitric acid, assuming that the nitric oxide can all be reconverted to nitric acid. The hydrocarbon that is not nitrated is converted to alcohols, carboxylic acids, aldehydes, ketones, carbon monoxide, carbon dioxide, and water. This oxidative reaction requires about 7 moles of nitric acid for each mole of butane. Based on the absence of HNO_3 and

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[1] McCLEARY with DEGERING, *Ind. Eng. Chem.*, **30**, 64 (1938).

NO_2 in the exit vapors, about 60 per cent of the nitric acid is used as oxidizing agent; consequently, one-seventh of 60 per cent or 0.08 mole of hydrocarbon is oxidized by the nitric acid for each mole of nitric acid reacting. The percentage of hydrocarbon nitrated is therefore approximately $(0.40 \times 100)/(0.40 + 0.08)$ or 83 per cent. In commercial operations where the nitric oxide is separated from other reaction products and is reoxidized to nitric acid, up to 90 moles of nitroparaffins can be produced for each 100 moles of nitric acid consumed.

Nitric acid can be produced by the oxidation of ammonia at a cost of approximately 1.75 cts. per pound on an anhydrous basis. Butane is available at about 0.6 ct. per pound. The raw material cost of a pound of crude, nitrated butane, using the above figures, is approximately 1.8 cts. per pound. Natural gas which consists of approximately 85 per cent methane is available in certain fields at about 4 cts. per 1,000 cu. ft. (44 lb.). Natural gas is also the preferred source of hydrogen for the production of synthetic ammonia. As a result of recent developments, it is altogether probable that nitromethane and its numerous derivatives (see page 8) may become available on any desired scale and at relatively low costs.

IX. THERMAL DATA RELATING TO THE PREPARATION AND USE OF NITRO COMPOUNDS

From the previous paragraphs, it has become apparent that the nitration process is accompanied by the development of a considerable amount of heat. A discussion of nitration processes would therefore be incomplete without taking into consideration some of the thermal factors involved in this reaction.

Garner and Abernethy found (Figs. 16, 17) that certain regularities exist between the heats of formation and nitration of the benzene, toluene, and phenol series.[1] The heats of nitration decrease with the increase in the number of nitro groups, but the heats of formation tend to a maximum for the second or third member of the series and then diminish. An exception is seen in the benzene series, but it is probable that the maximum is shifted to the fourth member of the series and that the same relationship would hold if the more highly nitrated benzenes could be obtained.

In the benzene, toluene, and phenol series, it is clear (Tables IX, X, XI) that the nearer the nitro groups are to one another in the benzene ring the greater is the strain in the molecule and the lower the heat of formation. Thus *o*-dinitrobenzene and the ortho mononitro compounds of the toluene and phenol series have the smallest heats of formation. The differences between the ortho and para derivatives are, however, greatest for the benzene and least for the phenol series. In the case of di- and trinitro derivatives also, the proximity of the groups has the same effect.

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[1] Garner and Abernethy, *Proc. Roy. Soc.* (*London*), **99A**, 213 (1921), from which the following paragraphs were abstracted. The work of Rinkenbach of the Picatinny Arsenal [*J. Am. Chem. Soc.*, **52**, 115 (1930)] is also an important study in this field.

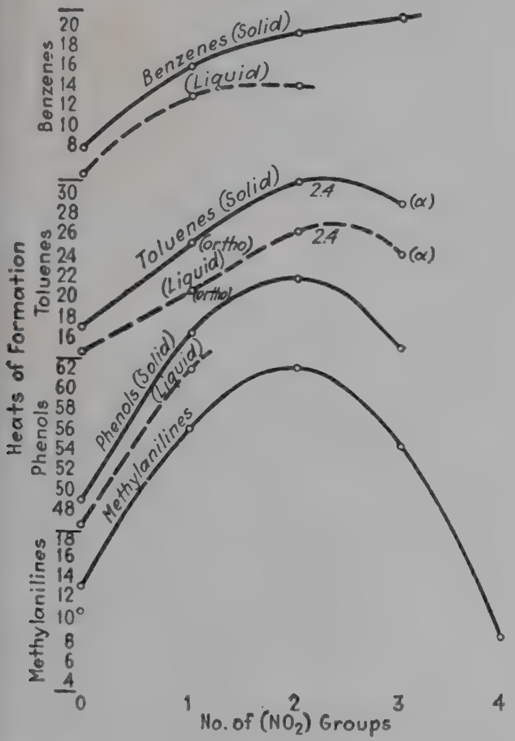

FIG. 16.—Heats of formation (kg. cal. per mole).

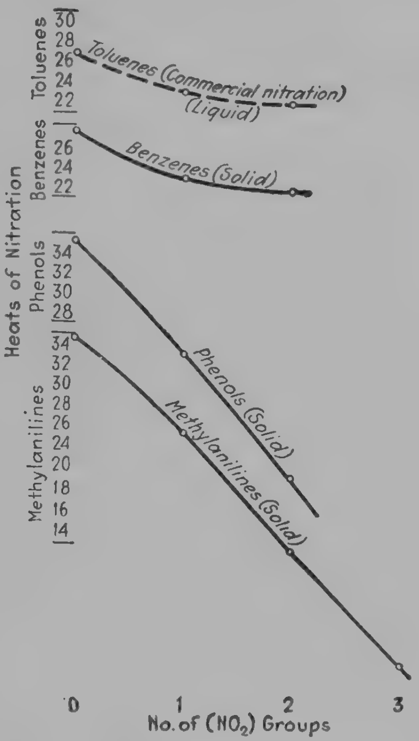

FIG. 17.—Heats of nitration (kg. cal. per mole).

TABLE IX.—HEATS OF COMBUSTION, FORMATION, NITRATION, AND CRYSTALLIZATION
Benzene Series

Substance	Mol. wt.	Heat of combustion, kg. cal. per mole		Heat of formation, kg. cal. per mole		Heat of nitration, kg. cal. per mole	Heat of crystallization, kg. cal. per mole
		Const. vol.	Const. press.	C. amorph.	C. diamond		
Benzene	78	780.4	781.3	+ 5.6	−10.6	+27.0	2.35
Nitrobenzene	123	739.9	739.7	+13.1	− 3.1	+25.6	2.78
o-Dinitrobenzene	168	703.8	702.6	+16.0	− 0.2		
m-Dinitrobenzene	168	700.6	699.4	+19.2	+ 3.0	+21.4	4.87
p-Dinitrobenzene	168	693.7	692.5	+26.1	+ 9.9		
1, 3, 5-Trinitrobenzene	213	665.6	663.4	+21.1	+ 4.9		
1, 2, 4-Trinitrobenzene	213	675.9	673.7	+10.8	− 5.4		

Some regularities have been observed in the heats of formation of members of the toluene series. Thus, there appears to be a definite *increase* in the internal energy (lower value for heat of formation) associated with groups in the ortho position, and especially when nitro groups are ortho to one another. Thus, of the isomeric trinitrotoluenes, β-(2, 3, 4) trinitrotoluene (Table XI) has the lowest heat of formation, *i.e.*, contains the greatest internal energy per gram; and α-(2, 4, 6) trinitrotoluene the highest heat of formation, *i.e.*, contains the least internal energy per gram. If on detonation these two substances gave the same products of decomposition, β-trinitrotoluene would have an advantage over α-trinitrotoluene of 54 cal. per gm. For the same reason, the unsymmetrical trinitrobenzene should be a more powerful explosive than the symmetrical body. In general, the greater the number of adjacent groups in a molecule of high explosive the greater will be the heat of detonation, but there are often practical limitations to this choice on account of the greater reactivity and lower stability of the less symmetrical nitro compounds.

TABLE X.—HEATS OF COMBUSTION, FORMATION, NITRATION, AND CRYSTALLIZATION

Phenol Series

Substance	Mol. wt.	Heat of combustion, kg. cal. per mole		Heat of formation, kg. cal. per mole		Heat of nitration, kg. cal. per mole	Heat of crystallization, kg. cal. per mole
		Const. vol.	Const. press.	C. amorph.	C. diamond		
Phenol	94	736.9	737.5	+49.4	+33.2	+35.0	2.34
o-Nitrophenol	139	689.9	689.4	+63.4 } 64.9	+47.3 } 48.7	+24.5	4.30
p-Nitrophenol	139	687.0	686.5	+66.3	+50.1		
2, 4-Dinitrophenol	184	650.2	648.7	+69.9	+53.7	+12.9	
Picric acid	229	623.7	621.2	+63.3	+47.1		

X. RECOVERY OF SPENT ACID FROM NITRATIONS[1]

The economical recovery and utilization of the large amounts of spent acids necessarily produced as a by-product in the manufacture of nitrohydrocarbons or other organic compounds are problems of great importance. In the early days of the synthetic organic chemical industry, practically all the spent acid was wasted. In the course of time, however, the disposition of nitration spent acid became an acute problem, for the continued pollution of streams constituted a serious menace. Thus, as in the case of waste SO_2 fumes from the smelters, a new industry was born of legal necessity. Later, economic reasons brought further pres-

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[1] Acknowledgment is made of the following sources of information: MARX, *Chem. Age*, **29**, 253 (1921); WEBB, *J. Soc. Chem. Ind.*, **40**, 265 (1921); ZEISBERG, *Chem. Met. Eng.*, **30**, 781 (1924).

TABLE XI.—SUMMARY OF HEATS OF COMBUSTION, FORMATION, AND NITRATION PER MOLECULE, AND FIGURES OF INSENSITIVENESS

Substance	Mol. wt.	Heat of combustion (kg. cal. per mole)		Heat of formation (kg. cal. per mole)		Heat of nitration, kg. cal. per mole			Heat of crystallization (kg. cal. per mole)	Gas evolution at 120°C. c.c. per 40 hr.	Figure of insensitiveness (picric acid = 100)
						One NO_2 group inserted in the following positions relative to existing NO_2 groups					
		Const. vol.	Const. press.	C. amorph.	C. diamond	Ortho position	Meta position	Para position			
Toluene	92	935.9	937.1	+15.1	− 3.8	+25.3	+29.4	+33.7	2.4		
Mononitrotoluene:											
Ortho (liquid)	137	897.0	897.2	+20.9	+ 2.0	2:3+22.9	2:4+29.7 2:6+28.2	2:5+27.3			
Meta (liquid)	...	892.9	893.1	+25.0	+ 6.1	2:3+18.8 3:4+18.5	3:5+25.4	2:5+23.2	4.3		
Para	...	888.6	888.8	+29.3	+10.4	3:4+14.2	2:4+21.3				
Dinitrotoluene:											
2:3	182	860.5	859.6	+24.3	+ 5.4	2:3:4+12.1	2:3:5+21.2	2:3:6+19.7 2:3:5+21.2			
2:4	...	853.7	852.8	+31.1	+12.2	3:4:6 12.6 2:3:4 5.3	2:4:6 17.5	3:4:6 12.6	4.80		
2:5	...	856.1	855.2	+28.7	+ 9.8	2:3:5 16.8 3:4:6 15.0 2:3:6 15.3	2:3:5 16.8 3:4:6 15.0 2:3:6 15.3				
2:6	...	855.2	854.3	+29.6	+10.7	2:3:6 14.4	2:4:6 19.0	2:3:6 14.4			
3:4	...	860.8	859.9	+24.0	+ 5.1	2:3:4 12.4 3:4:5 17.2	3:4:6 19.7	3:4:6 19.7			
3:5	...	853.9	853.0	+30.9	+12.0	2:3:5 14.6 3:4:5 10.8	....	2:3:5 14.6			
Trinitrotoluene:											
α (2:4:6)	227	822.5	820.7	+20.1	+10.2	....	....	....	4.88	0.08	114
β (2:3:4)	...	834.7	832.9	+16.9	− 2.0	....	....	....	....	0.73	92
γ (3:4:6)	...	827.4	825.6	+24.2	+ 5.3	....	....	....	....	1.40	102
δ (3:4:5)	...	829.9	828.1	+21.7	+ 2.8	....	....	....	....	1.60	95
ε (2:3:5)	...	825.6	823.8	+26.0	+ 7.1	....	....	....	....	0.40	101
ζ (2:3:6)	...	827.1	825.3	+24.5	+ 5.6						

sure to bear, so that at present a number of satisfactory means are available for effecting both the recovery and concentration of spent acids from nitrations.

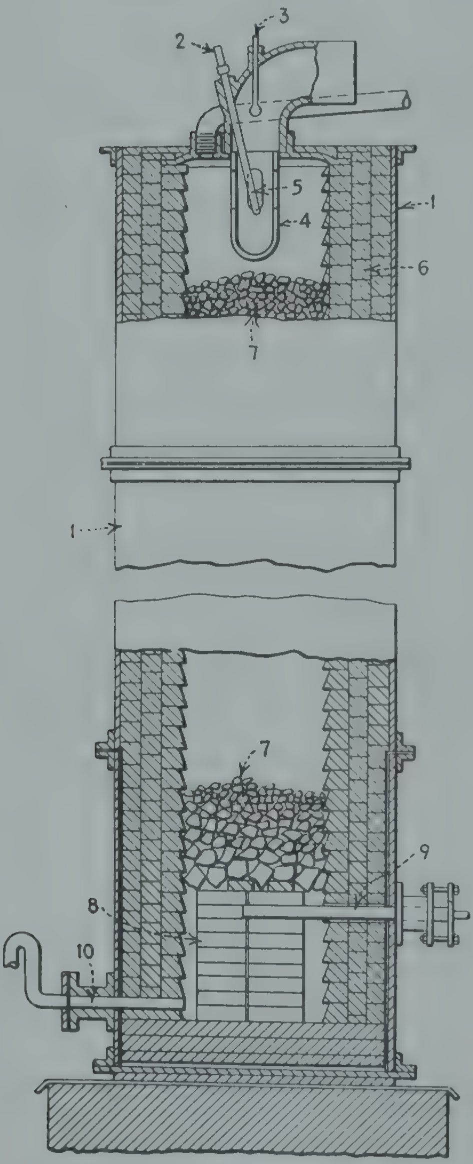

FIG. 18.—Denitrating tower.

1. Steel shell for denitrating tower.
2. Spent acid delivery.
3. Thermometer.
4. Distributor for spent acid.
5. Openings for HNO_3 vapors.
6. Inner brick lining.
7. Chemical ware packing.
8. Tiles, arranged in checkered layers.
9. Steam inlet.
10. Outlet for denitrated sulfuric acid.

In normal times, there are but two principal sources of spent nitrating acids—those from the nitration of aromatic compounds, such as benzene, chlorobenzene, toluene, or phenol, and those resulting from the esterification of glycerol and the carbohydrates cellulose, starch, and sugar. While the spent acids from the former consist of sulfuric acid with but minimal amounts of nitric acid and relatively large amounts of water, those from the latter source contain many times more nitric acid and therefore are first denitrated before being delivered to the sulfuric acid concentrating plant.

In many areas of the country, the spent acid from the nitration of hydrocarbons as well as the **denitrated** spent acid from the nitration of phenols and polyhydric alcohols can be sold to the producers of superphosphate fertilizers. The presence of small amounts of chemical N or of organic matter in the denitrated sulfuric acid constitutes no deterrent to its use as an acidulant for phosphate rock.

Denitration of Spent Acid.—The initial step in the recovery of spent acids consists in the removal of the residual nitric and nitrous acids from the bulk of diluted sulfuric acid. The nitrous acid in spent acid is, however, not present as HNO_2 but as nitrosylsulfuric acid $HO\cdot SO_2\cdot ONO$, since spent acid does not give many of the ordinary tests for nitrous acid unless diluted with water. The operating details relating to the recovery of the nitrogen compounds in spent acid must therefore be preceded by a study of their reactions

Nitrosylsulfuric acid ($HO \cdot SO_2 \cdot ONO$) is quite stable in the presence of concentrated sulfuric acid. In concentrations below 70 per cent H_2SO_4, the velocity of decomposition is much greater, increasing with the temperature and dilution of the sulfuric acid; *e.g.*, in 72.8 per cent H_2SO_4, considerable decomposition occurs at 100°C.; at 68.5 per cent, the whole of nitrosylsulfuric acid is decomposed at the boiling point of the solution; whereas with acids of concentration below 64.26 per cent H_2SO_4, crystals of nitrosylsulfuric acid do not dissolve in the cold without decomposition.

In order to effect complete separation of nitrous and nitric acid from mixtures with sulfuric acid, it is necessary first to dilute the mixture until the concentration of the sulfuric acid is about 70 per cent and then to heat the same to a sufficiently high temperature to drive off the volatile constituents. The resulting vapors of nitric acid are condensed while the nitrous gases, consisting essentially of NO and NO_2, are absorbed in dilute nitric acid of 35 to 55 per cent strength, the final oxidation of the absorbed gases being effected by admixture and agitation with atmospheric oxygen.

These operations are best carried out in denitration towers constructed of acid-resistant material. The spent acid is delivered to a distributor on top of the tower (Fig. 18) and is allowed to trickle down through the packing while being subjected to an ascending current of saturated or superheated steam, the steam serving both to dilute the mixture and to drive off the nitric acid.

The reactions that take place may be summarized as follows: Spent acid entering the top of the tower is heated by escaping oxides of nitrogen, and any nitric acid present is decomposed by nitrosylsulfuric acid with the formation of NO_2 according to the following reversible reaction:

$$HNO_3 + HO \cdot SO_2 \cdot ONO \rightleftarrows H_2SO_4 + 2NO_2 \qquad (1)$$

Farther down, the remaining nitrosylsulfuric acid is decomposed by steam.

$$2HO \cdot SO_2 \cdot ONO + H_2O \rightarrow 2H_2SO_4 + NO + NO_2 \qquad (2a)$$
$$HO \cdot SO_2 \cdot ONO + H_2O \rightarrow H_2SO_4 + HNO_2 \qquad (2b)$$

The nitrous acid thus formed is decomposed at the elevated temperatures that prevail, probably according to the following equations:

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \qquad (3)$$
$$3HNO_2 \rightleftarrows 2NO + HNO_3 + H_2O \qquad (4)$$

the nitric acid distilling off. The denitrated sulfuric acid, containing about 67 to 70 per cent H_2SO_4, which flows off from the bottom of the tower, will retain not over 0.15 per cent nitric acid and is suitable for concentration and reuse. The nitric acid in the gases leaving the tower is first led through a set of condensers where any nitric acid is liquefied and recovered, the noncondensable gases, consisting of NO and NO_2, passing on to an absorption system (Fig. 19) where they encounter a downward current of nitric acid, experience having shown that 55 per cent nitric acid possesses the maximum absorptive capacity. The air introduced through the pulsometers, *i.e.* air lifts, serves to oxidize the absorbed NO to NO_2, thus enriching the nitric acid. Enough air is added so as to provide about 3 per cent oxygen, the residual gases leaving the absorption system.

The strength of the recovered nitric acid from spent acids is greatly increased by returning the comparatively weak absorption-tower acid to the denitrating column.[1] In this way, the concentration of the nitric acid is increased from the usual 55 to 60 per cent strength to 90 per cent or more. The usual denitration and absorption system is employed (Fig. 19). This comprises a denitrating tower, a "bleaching" tower filled with disks or cylinders, an S bend condenser of high-silicon iron, and a series of absorption towers. The dilute acid that accumulates in the absorption system is pumped back to the top of the denitrating tower, where it is mixed with the spent acid as it enters the tower. The spent acid contains sufficient H_2SO_4 to combine with the H_2O of the absorption-tower acid to form nonvolatile hydrates of sulfuric acid under the conditions existing in the denitrating tower, thus permitting the HNO_3 content

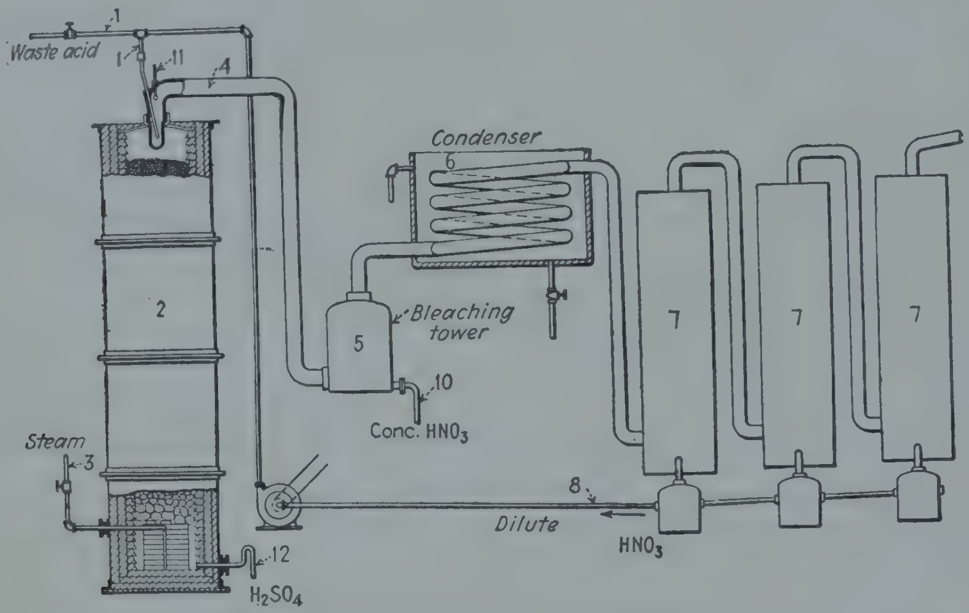

FIG. 19.—System for the production of concentrated nitric acid.

1. Spent acid delivery.
2. Denitrating tower.
3. Steam inlet.
4. Outlet for nitric acid vapors.
5. Bleaching tower.
6. Chemical ware condenser.
7. Absorption towers.
8. Dilute nitric acid—returned to denitrating tower.
10. Outlet for concentrated nitric acid.
11. Thermometer.
12. Outlet for diluted sulfuric acid.

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[1] U. S. 1,590,043 (1926).

of this acid to be vaporized in comparatively anhydrous condition from the top of the denitrating tower.

This scheme works satisfactorily only for spent acids that are comparatively free of dissolved hydrocarbons and in which the free HNO_3 content is two or more times that of the nitrosylsulfuric acid. The unsuitability of acids like trinitrotoluene spent acid is due to the excessive reduction of nitric acid that occurs at the top of the denitrating tower.

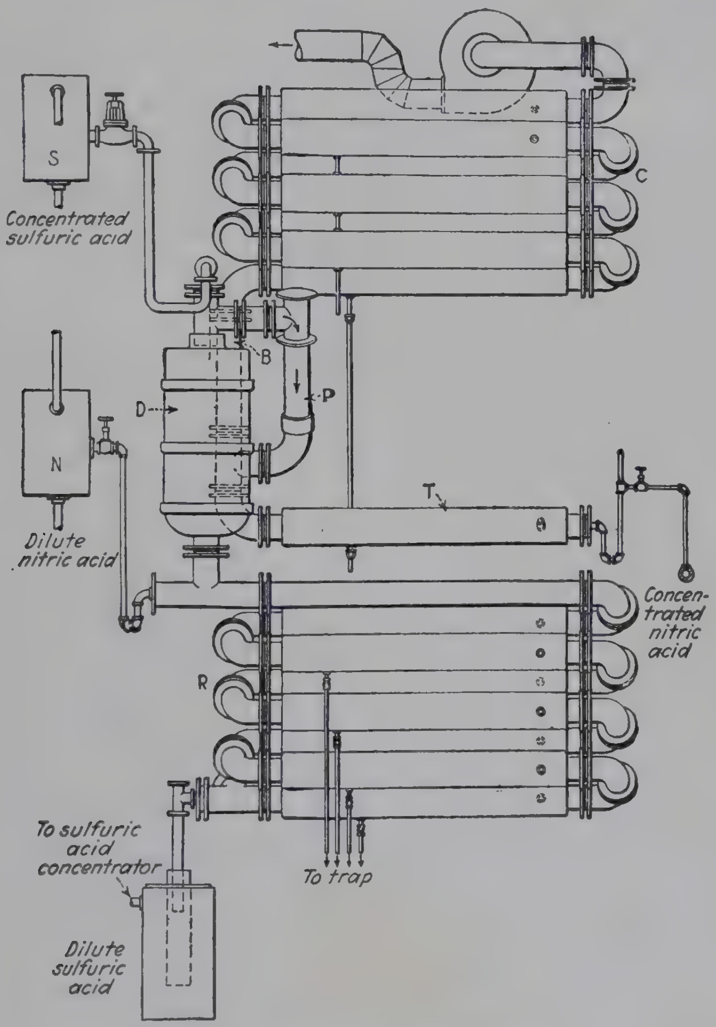
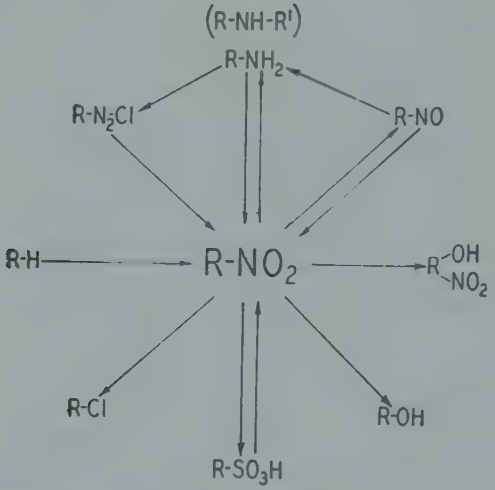

S
Concentrated sulfuric acid
C
B
D
P
N
Dilute nitric acid
T
Concentrated nitric acid
R
To sulfuric acid concentrator
To trap
Dilute sulfuric acid

Fig. 20.—Nitric acid concentrator.

Concentration of Nitric Acid.—The concentrating of dilute nitric acid obtained from denitration systems or ammonia-oxidation operations can be accomplished in a vertical tower in which the ternary mixture, nitric acid, sulfuric acid, and water, passes downward countercurrent to a hot gaseous medium composed largely of steam.

It is clear, however, that the direct contact of steam with the dehydrating sulfuric acid necessitates using larger quantities of this acid than would be required if the necessary heat were supplied through a heat exchanger. A large number of such improved concentrating systems have been devised.[1,2] These are of either the tower or the tubular type, and their performance indicates that the quantity of sulfuric acid required to concentrate a ton of 36°Bé. nitric acid (53 per cent) can thereby be reduced from 2.5 to 1.5 tons. The tubular equipment shown in Fig. 20 is an example of a modern economical nitric acid concentrating system.[3] Any vapors leaving the nitric acid condenser may be removed under reduced pressure and delivered to the concentrated sulfuric acid to be used for dehydration.[4]



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[1] U. S. 1,722,122 (1930); 1,920,307; 1,921,255; 1,922,278; 1,922,289; 1,924,312 (1933).

[2] Sillich, *Ind. Eng. Chem.*, **33**, 1248 (1941).

[3] U. S. 1,916,837 (1933).

[4] U. S. 1,920,307 (1933).

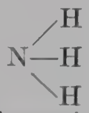
CHAPTER II

AMINATION BY REDUCTION

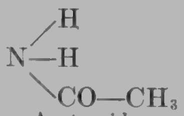
By P. H. Groggins

I. OUTLINE OF PROCESSES FOR THE PREPARATION OF AMINES

A compound containing the —NH_2 group united to a radical of acid character is called an amide, or an amido compound. An amine, or amino compound, is one containing the —NH_2 group united to a radical other than an acid radical. Acetanilide ($CH_3 \cdot CO \cdot NHC_6H_5$), formamide ($H \cdot CO \cdot NH_2$), and benzamide ($C_6H_5 \cdot CO \cdot NH_2$) are amido compounds, as they may be regarded as being derived from ammonia by the substitution of an acidic residue in place of hydrogen; *e.g.*,



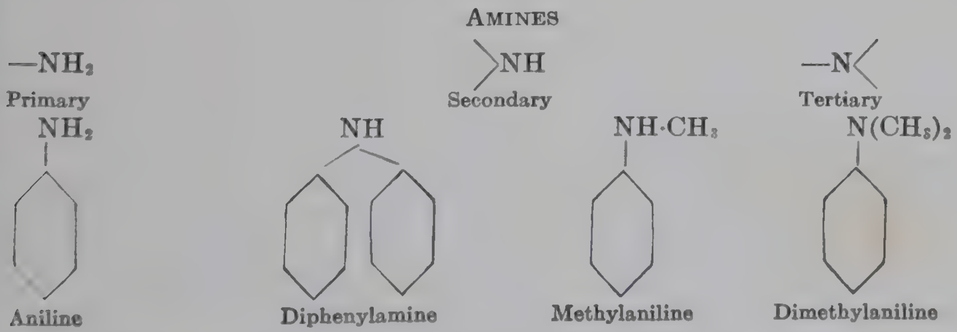
Ammonia



Acetamide

Aniline and 2-aminoanthraquinone are examples of amino compounds. The processes of preparing these compounds may be termed *amidation* and *amination*, respectively.

Amines are divided into three classes—primary, secondary, and tertiary—the distinguishing characteristic being the number of hydrogen atoms in the parent substance *ammonia* that have been replaced by organic radicals. The classification may be illustrated graphically as follows:



With respect to amination by reduction, the most important of these compounds are the aromatic primary amines, since they are almost invariably the starting materials for the preparation of amines of other classes.

A number of methods may be utilized for the preparation of amines, and oftentimes only a change in economic factors or the presence of patent barriers is responsible for the selection of a manufacturing technic for the production of a particular compound. Thus, aniline may be prepared commercially by the ammonolysis of chlorobenzene, the acid or alkaline reduction of nitrobenzene, or the catalytic hydrogenation of nitrobenzene in the vapor phase.

The methods generally used for the preparation of primary amines are the following:

1. The reduction of nitro compounds, also of the intermediate products of reduction, as the nitroso, azo, and hydrazo compounds.
2. Ammonolysis. The treatment of compounds containing labile nitro groups, sulfonic acid groups, hydroxy groups, carbonyl groups, or halogen atoms with ammonia.
3. The reduction of nitriles.
4. Intramolecular rearrangement of such compounds as secondary or tertiary amines, hydrazobenzenes, and hydroxylamine derivatives.
5. From amides, by hydrolysis or the action of alkaline hypochlorite.
6. The direct introduction of the amino group by means of agents other than ammonia.
    - *a.* Treatment with hydroxylamine in sulfuric acid solutions.
    - *b.* Fusion of polynitroaromatic compounds containing halogen atoms with urea, or other dibasic amides.
    - *c.* Treatment with *p*-toluenesulfonamide.

To ensure a proper balance in this work, only the two most important methods of amination are considered. The present discussion relates to amination by reduction; and later, in Chap. VI, the process of amination by ammonolysis is given consideration.

Aromatic and Aliphatic Compounds.—In this chapter, emphasis is placed on the reduction of aromatic rather than aliphatic nitro compounds. Such accentuation is considered desirable because (1) the arylnitro compounds are readily available and are used extensively for the technical preparation of arylamines; (2) the processes are generally susceptible to close control and give high yields; (3) the fundamental principles have been more exhaustively studied; and (4) the principles based on aromatic chemistry can to a considerable extent be applied in the treatment of aliphatic compounds. In Chap. VI, however, the preparation of alkylamines and other aliphatic amines are given adequate and merited consideration.

II. THE REDUCTION OF NITRO COMPOUNDS

Introduction.—The reduction of nitro compounds involves the progressive replacement of oxygen in the —NO_2 group by hydrogen. There are two groups of reduction products, *viz.*, the primary, which have one benzene ring; and the secondary, which contain two benzene rings. The intermediate compounds obtained from the reduction of nitrobenzene are shown in the accompanying chart.

Under suitable conditions, gaseous hydrogen in the presence of a metal catalyst, such as nickel, tin, platinum, or copper, may be used as the reducing agent. This method finds widespread and important application in the industrial synthesis of both aliphatic and aromatic amines. It is more frequently found most effective and economical to utilize the hydrogen liberated on metal surfaces by acid, alkaline, or neutral solution. Such *active* hydrogen possesses a larger amount of free energy than hydrogen gas.[1]

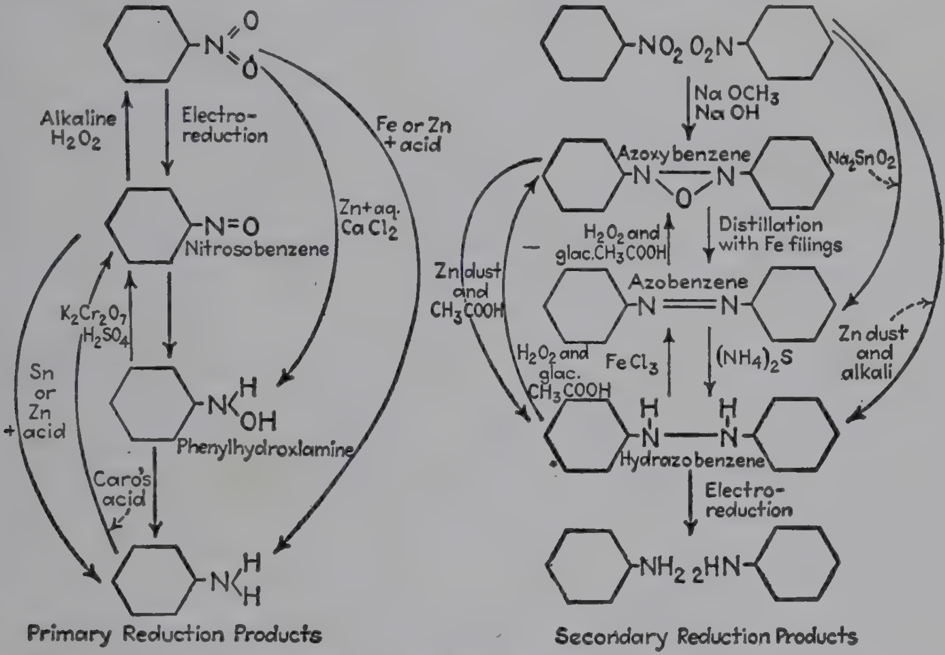

Alkaline H2O2
Electro-reduction
Fe or Zn + acid
Zn+aq. CaCl2
Nitrosobenzene
K2Cr2O7 H2SO4
Sn or Zn + acid
Phenylhydroxlamine
Caro's acid
Primary Reduction Products
Na OCH3 Na OH
Azoxybenzene
Na2SnO2
H2O2 and glac.CH3COOH
Distillation with Fe filings
Zn dust and CH3COOH
Azobenzene
Zn dust and alkali
H2O2 and glac. CH3COOH
FeCl3
(NH4)2S
Hydrazobenzene
Electro-reduction
Secondary Reduction Products

FIG. 1.—Reduction of nitrobenzene: intermediate products.

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[1] The term *active* hydrogen is used by Prins, Haber, and others, as we have used it above, to mean hydrogen activated by contact with a metal. There seems to be no question that contact with different metals confers on free hydrogen the ability to produce different chemical changes in the same substance. Thus, hydrochloric acid and some nitric acid with zinc give ammonia; with magnesium, no ammonia; with tin, ammonia and hydroxylamine. Here the hydrogen is the same, but the metallic contact agent is different, and the free energy of the acid with each metal is different. If, now, hydrogen gas is led through the cold nitric acid solution, little or no action occurs. To explain the apparently greater activity of the hydrogen in the first three experiments, we note the fact that the hydrogen is liberated on the surface of the metals. The activity of the hydrogen liberated by the hydrolysis of salts in the presence of metals or by the action of acids on metals is "due to the larger amount of free energy contained in zinc plus acid plus reducible substance as compared with the free energy contained in free hydrogen plus reducible substance."

In a similar manner, it can be shown that the oxygen liberated in the decom-

Since *active* hydrogen can be produced by diverse reactions, it follows that reductions may be accomplished by many methods. It is important to bear in mind that the metals iron, tin, and zinc, which are customarily employed in reduction processes, each have characteristic properties when used in acid or alkaline solutions. Conditions must therefore be chosen with respect to the compound to be treated and the degree of reduction desired.

By controlling the reducing activity of the system, *i.e.*, by regulating the energy potential at which hydrogen is liberated, it is possible to obtain intermediate products of reduction from nitro compounds. In the chart (Fig. 1) are shown the reduction products of nitrobenzene, and below is given the value of potentials of reducing agents with reference to the normal hydrogen electrode using platinum poles.

$SnCl_2$ in KOH	0.861 volt	Hydrogen in HCl	0.311 volt
Na_2S	0.651 volt	I_2 in KOH	0.070 volt
Hydroxylamine in KOH	0.616 volt	$SnCl_2$ in HCl	0.064 volt

Nitrosobenzene can be obtained by electroreduction of nitrobenzene.

Phenylhydroxylamine is obtained by treating an alcoholic solution of nitrobenzene with zinc dust and a small quantity of calcium chloride.

Azoxybenzene is produced by boiling nitrobenzene with an alcoholic solution of potassium hydroxide. A whole series of azoxy compounds has been prepared by reducing nitrotoluene, *p*-nitrochlorobenzene, etc., in alcoholic solution with ammonium chloride and magnesium.[1]

Azobenzene can be obtained by distilling azoxybenzene in the presence of finely divided iron. When nitrobenzene is reduced with a solution containing Na_2SnO_2 made from stannous chloride in an excess of sodium hydroxide, a partial reduction to the azo stage is obtained. In hydrochloric acid solution, stannous chloride converts the nitro compound to the amino derivative.

Hydrazobenzene is formed when nitrobenzene is reduced by zinc dust in alkaline solution. The presence of alkali is necessary; as in neutral solution, phenylhydroxylamine is formed; and in acid solution, aniline is the reduction product.

Outline of Methods.—The most useful methods for carrying out the reduction of nitro compounds are the following:

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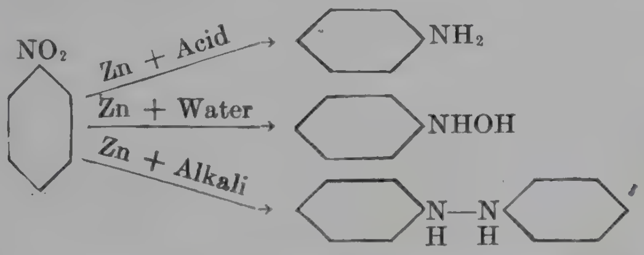
position of hypochlorous acid is a more active oxidizing agent than is free oxygen gas. Thus, the heat liberated in the oxidation of indigo to isatin by oxygen gas, if it could be carried out, would be 1,800 cal. The much greater heat liberated when hypochlorous acid is used is obtained by adding the thermochemical equations."

$$2HClO = 2HCl + 2O + 18{,}600 \text{ cal.}$$
$$C_{16}H_{10}N_2O_2 + 2O = 2C_8H_5NO_2 + 1{,}800 \text{ cal.}$$
$$C_{16}H_{10}N_2O_2 + 2HClO = 2C_8H_5NO_2 + 2HCl + 20{,}400 \text{ cal.}$$

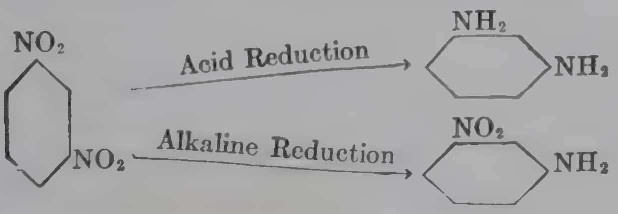
[1] Ger. 446,867 (1924).

1. Iron, tin, and zinc—in the presence of water and (*a*) certain mineral or organic acids, (*b*) sulfur dioxide, (*c*) salts, particularly those derived from the neutralization of strong acids.
2. Zinc and iron in the presence of solutions of the strong alkalies.
3. Alkali or metal sulfides in solution or suspension as dilute sodium, calcium, ammonium, manganese, or iron sulfides.
4. Ferrous sulfate in alkaline solution.
5. Hydrogenated bases of the quinoline series.
6. Sodium hydrosulfite in alkaline solution.
7. Gaseous hydrogen or mixtures thereof with carbon monoxide in the presence of a catalyst (*a*) in alkaline solution, (*b*) in vapor phase.
8. Paraffins and cycloparaffins in the presence of a base metal hydrogenation catalyst.

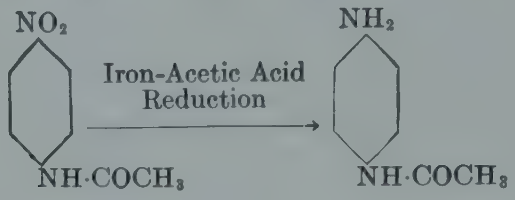
By a proper selection of the reducing agents and careful regulation of the process, the reduction may be stopped at intermediate stages, and valuable products other than amino compounds may thus be obtained. The metal-acid reductions are the most vigorous, and only amino compounds are obtained as end products. When nitrobenzene is treated with zinc and a mineral acid solution, the end product is aniline; when an alkaline solution is employed, the end product is hydrazobenzene. When zinc dust and water are employed, the reaction product is phenylhydroxylamine. The following structural formulas represent the three modifications of this reduction process:



When the compound to be treated contains more than one nitro group, the products of reduction depend on the agents used; thus, *m*-phenylenediamine is obtained by the iron-acid reduction of *m*-dinitrobenzene, while the alkaline sulfide reduction yields *m*-nitroaniline.



Under certain conditions, the mineral acid is replaced by an organic acid—acetic acid. This is essential in order to avoid decomposition in the treatment of complex compounds, *e.g.*, nitroaminobenzoylbenzoic acids, and also in the reduction of nitroanilides, for here



the presence of hydrochloric acid would tend to hydrolyze the anilide to a nitroamino compound.

III. REDUCTION WITH IRON IN ACID OR NEUTRAL SOLUTIONS

Theory and Mechanism of the Reaction.—Béchamp's discovery in 1854 that nitro compounds could be reduced in the presence of iron and acetic acid and Perkin's subsequent application in 1857 of this reaction for the commercial preparation of aniline were events of great significance for the development of the dye industry. Technical progress in the application of this reaction was first made by substituting hydrochloric acid for the acetic acid originally employed. Subsequently, it was discovered that the ferrous salt of the acid functioned catalytically, so that the reduction could be effected with less than the theoretical quantity of acid.

Considerable discussion has taken place in explaining the consumption of less acid than the quantity theoretically required, when the reduction is represented as taking place as follows.

$$\begin{array}{lcccccc} & C_6H_5NO_2 & + & 2Fe & + & 6HCl \rightarrow C_6H_5NH_2 + 2H_2O + 2FeCl_3 \\ \text{Mol. wts.} & 123 & & 2(55.84) & & 6(36.45) \end{array}$$

In industrial practice, less than 2 per cent of the amount indicated above is actually used. Operating experience has shown that 3.0 lb. of hydrochloric acid (10 lb. of 30 per cent solution) is required to bring about a satisfactory reduction of 100 lb. of nitrobenzene to aniline.

The presence of free acid, which was long considered essential to the reduction process, has furthermore been shown to be no longer necessary. In 1914, von Girsewald showed that ferrous chloride could be used as the catalytic agent in the reduction process.[1] Moore subsequently demonstrated that sodium chloride could be employed in the reduction of nitrosophenols and *p*-nitroacetanilide to the corresponding amino and amido derivatives.[2] This investigator found also that sodium chloride was not nearly so active as calcium chloride for this purpose.

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[1] Girsewald, Ger. 281,100 (1914).

[2] Moore, Brit. 155,319 (1919).

Within recent years, it has been demonstrated that aniline hydrochloride, aluminum chloride, sodium bisulfate, or other salts derived from strong acids can be successfully employed. It is merely essential to use such salts that in the presence of metals are hydrolyzed in aqueous solutions resulting in the formation of hydrogen ions.

Theory of Reaction.—A number of investigators have advanced theories to explain the catalytic iron-salt reduction process. To appreciate better these explanations, it is interesting first to follow the role that iron plays in providing the active hydrogen for the reduction process.

Alexander and Byers have established that hydrogen is generated when a mill containing iron balls and water is rotated at room temperatures.[1] Bergius has shown that pure hydrogen can be continuously generated from iron and water at 200 to 300°C.[2] He has also found that common salt, iron chloride, or small quantities of hydrochloric acid greatly accelerate the reaction and that the iron is converted almost entirely to ferrosoferric oxide.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Magnetic iron oxide is the final product of oxidation, the intermediate products being presumably ferrous and ferric hydroxides.

Chemical Mechanism.—In considering the chemical behavior of the amines, it is found that these compounds dissociate on solvation only to a slight extent, thereby forming a weak base.

$$C_6H_5NH_2 + HOH \rightleftharpoons (C_6H_5NH_3)OH \rightleftharpoons (C_6H_5NH_3)^+ O\overset{-}{H}$$

The salts of aniline, like those of all primary benzenoid amines, are easily hydrolyzed. Compared with alkylamines, the aromatic amines are comparatively weak bases, and their salts with mineral acids are quite acidic.

In the following equations, an attempt is made to present an outline of the iron-acid reduction process based on certain facts relating to the oxidation of the iron, the hydrolysis of neutral salts, and the dissociation of amines. The representation is admittedly incomplete in many of the details, particularly with respect to Eqs. (5) to (8) relating to the progressive oxidation of the iron.

$$(FeCl_2)Fe + 2H_2O \rightarrow (FeCl_2) + Fe(OH)_2 + H_2 \qquad (0)$$

$$R{\cdot}NO_2 + (FeCl_2) + 3Fe + 4H_2O \rightarrow R{\cdot}NH_2 + (FeCl_2) + 3Fe(OH)_2 \qquad (1)$$

$$R{\cdot}NH_2 + H_2O \rightarrow (R{\cdot}NH_3)OH \rightarrow (R{\cdot}NH_3)^+ + O\overset{-}{H} \qquad (2)$$

$$2R{\cdot}N\overset{+}{H}_3 + 2O\overset{-}{H} + \overset{++}{Fe} + 2C\overset{-}{l}^{-} \rightarrow 2R{\cdot}NH_3Cl + \underset{\text{Limited Solubility}}{\underline{Fe(OH)_2}} \qquad (3)$$

$$2R{\cdot}N\overset{+}{H}_3 + 2C\overset{-}{l} + Fe \xrightarrow{H_2O} 2R{\cdot}NH_2 + FeCl_2 + H_2 \qquad (4)$$

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[1] ALEXANDER and BYERS, *J. Chem. Education*, **9**, 916 (1932).

[2] Bergius, U. S. 1,059,818 (1913).

Formula (0) merely expresses the preliminary action between iron powder and water in the presence of an acid or salts derived from strong acids. This activity, as Bergius has shown, is accelerated at higher temperatures and pressures. When a nitro compound is introduced [Eq. (1)], the active hydrogen does work in the reduction process. Equation (2) represents the formation of the weak base through solvation. The intermediate catalytic step is expressed by Eq. (3). The reactions indicated by the second and third equations show that aniline behaves similarly to ammonia. It unites with water to form the weakly dissociated base phenylammonium hydroxide, which, like ammonium hydroxide, precipitates the hydroxides of the heavy metals from solutions of their salts.

It is interesting to note that the ferrous ion which is essential to the reduction process is not present in the products of Eq. (3). In this connection, it has been observed that only a faint test for soluble iron can be obtained by spotting on filter paper with sodium sulfide solution directly after feeding considerable nitro compound to the reducer. When, however, reduction is complete, qualitative or spot tests show very distinctly the presence of soluble iron. From Eqs. (3) and (4), it may reasonably be inferred that the quantity of ferrous chloride catalyst should be proportional to the amount of amine that is dissociated, a slight excess being necessary in order to ensure an acid reaction. This is a matter of considerable practical importance in order that maximum yields and purity of product may be obtained. It has previously been shown that nitrobenzene may yield directly hydrazobenzene, phenylhydroxylamine, or aniline, depending on the hydrogen-ion concentration of the solution. The production of primary amines in this type of reduction necessitates a slight but definite acidity.

The reaction shown in Eq. (4) is the driving force in the reduction process, and the end products are in accordance with those observed under actual operating conditions. The primary amine is set free, and the ferrous chloride is regenerated for further catalytic activity.

When the reduction of nitrobenzene is carried out in a glass vessel, the early formation of a greenish precipitate, characteristic of ferrous hydroxide [Eq. (1)], is observed. This turns to a brown and finally to a black color, which suggests that the formation of the end product—magnetic iron oxide (Fe_3O_4)—is a secondary effect resulting from the reaction of ferrous hydroxide with ferric hydroxide.

The formation of magnetic iron oxide can reasonably be explained by assuming that the ferrous hydroxide initially formed executes a limited reducto-active role in the process and, as a result, is oxidized by the nitro compound.

$$R{\cdot}NO_2 + 2Fe(OH)_2 + H_2O \rightarrow R{\cdot}NO + 2Fe(OH)_3 \tag{5}$$

$$R{\cdot}NO_2 + 2Fe(OH)_2 + 2H_2 \xrightarrow{H_2O} R{\cdot}NH_2 + 2Fe(OH)_3 \tag{6}$$

If the intermediate catalytic reactions are eliminated and consideraion is given to the fact that the initially formed ferrous hydroxide is ontinuously undergoing oxidation and dehydration, Eq. (1) above may now be rewritten as a condensed picture of the reduction process.

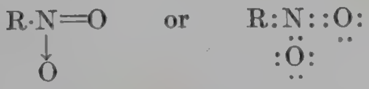
$$R{\cdot}NO_2 + 3Fe + 4H_2O \xrightarrow{FeCl_2} R{\cdot}NH_2 + Fe(OH)_2 + FeO + Fe(OH)_3 + \tfrac{1}{2}H_2 \quad (7)$$

$$Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O \quad (8)$$

Inasmuch as $2Fe(OH)_2$ serves in lieu of H_2 [Eqs. (5) and (6)], apparently only slightly over 2 moles of iron per mole of nitro compound are needed to give the end products shown in Eqs. (7) and (8).

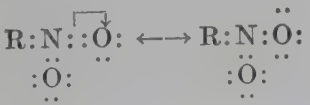
Electronic Mechanism.—According to Luder and Zuffanti,[1] the use of iron and acids to reduce nitrobenzene to aniline can be explained as follows: Any acid (using the word in the Lewis sense) will increase the concentration of hydrogen ions (hydrated of course) in a water solution.[2] The substances mentioned above are acids in this general sense. With iron and these acids in water solution, a plentiful supply of both electrons and protons is available.

According to the electronic theory, the nitro group is electrophilic and accepts electrons from the iron. The usual methods of writing the formula of nitrobenzene fail to indicate this electrophilic nature of the nitrogen atom:



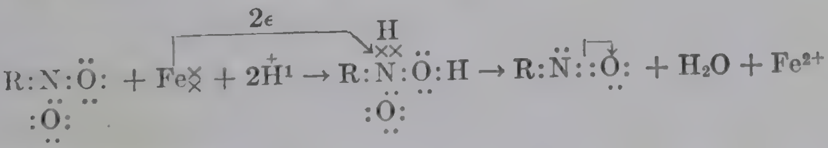
$$R{\cdot}\underset{\underset{O}{\downarrow}}{N}{=}O \qquad \text{or} \qquad R{:}\underset{:\ddot{\underset{..}{O}}:}{\ddot{N}}{::}\underset{..}{O}{:}$$

The nitrogen atom is bound to be electrophilic because of the pull on its electrons by the phenyl group and the two oxygen atoms. If this is indicated by the following device, we can picture the reduction of nitrobenzene to aniline a little more clearly:



$$R{:}\underset{:\ddot{\underset{..}{O}}:}{\ddot{N}}{::}\underset{..}{O}{:} \longleftrightarrow R{:}\underset{:\ddot{\underset{..}{O}}:}{\ddot{N}}{:}\overset{..}{\underset{..}{O}}{:}$$

The second formula emphasizes the electrophilic nature of the nitrogen atom by showing only 6 electrons on it. In the presence of iron and $\overset{+}{H}{}^{1}$ ions, we picture the first step in the reduction as an almost simultaneous addition of 2 electrons (from the iron) and 2 protons to the nitro group:



$$R{:}\underset{:\ddot{\underset{..}{O}}:}{N}{:}\overset{..}{\underset{..}{O}}{:} + Fe\overset{\times}{\underset{\times}{}} + 2\overset{+}{H}{}^{1} \xrightarrow{} R{:}\underset{:\ddot{\underset{..}{O}}:}{\overset{H}{\overset{\times\times}{N}}}{:}\overset{..}{\underset{..}{O}}{:}H \rightarrow R{:}\ddot{N}{::}\underset{..}{O}{:} + H_2O + Fe^{2+}$$

2ε

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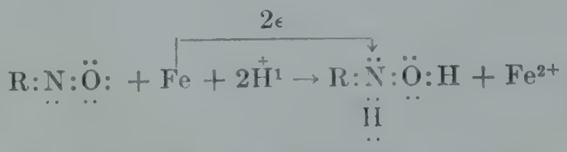
[1] Private communication.

[2] LUDER and ZUFFANTI, "Catalysis from the Viewpoint of the Electronic Theory of Acids and Bases," *Chem. Rev.*, **34**, 346 (1944).

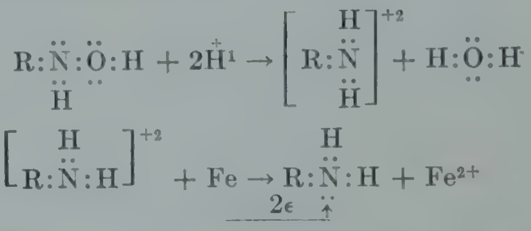
According to this picture, the evolution of hydrogen during the reduction is merely the result of a side reaction between the iron and hydrogen ions. The older chemical interpretation assumes that the hydrogen formed in contact with metals is responsible for the reduction. But breaking down a hydrogen molecule requires a large amount of energy. According to the electron theory, such a roundabout hypothesis is unnecessary, since electrons and protons are readily available from the iron and the acid solution.

The second step is the formation of phenylhydroxylamine by the same process as assumed in the first step:



$$\mathrm{R{:}\underset{..}{N}{:}\underset{..}{\ddot{O}}{:}} + \mathrm{Fe} + 2\overset{+}{\mathrm{H}}{}^1 \rightarrow \mathrm{R{:}\underset{\underset{..}{H}}{\ddot{N}}{:}\underset{..}{\ddot{O}}{:}H} + \mathrm{Fe}^{2+} \qquad (2\epsilon)$$

The third step is essentially the same but is shown in two parts to aid in picturing the details:



$$\mathrm{R{:}\underset{H}{\ddot{\underset{..}{N}}}{:}\underset{..}{\ddot{O}}{:}H} + 2\overset{+}{\mathrm{H}}{}^1 \rightarrow \left[\mathrm{R{:}\overset{H}{\underset{H}{\ddot{\underset{..}{N}}}}}\right]^{+2} + \mathrm{H{:}\underset{..}{\ddot{O}}{:}H}$$

$$\left[\mathrm{R{:}\overset{H}{\ddot{N}}{:}H}\right]^{+2} + \mathrm{Fe} \xrightarrow[2\epsilon]{} \mathrm{R{:}\overset{H}{\ddot{\underset{..}{N}}}{:}H} + \mathrm{Fe}^{2+}$$

Discussion of Mechanisms.—Depending on the mechanism that is accepted, the reduction of 1 mole of nitrobenzene requires 6 protons or 3 moles of hydrogen.

$$\mathrm{R{\cdot}NO_2} + 3\mathrm{H_2} \rightarrow \mathrm{R{\cdot}NH_2} + 2\mathrm{H_2O}$$

The reduction of 1 lb. of nitrobenzene would require $6 \div 123 = 0.049$ lb. of hydrogen. Using 0.0053 lb. per cu. ft. (188.8 cu. ft. per lb.) as a factor, we have $0.049 \div 0.0053 = 9.25$ cu. ft. of hydrogen as a requirement.

Hydrogen is evolved, and its presence creates a problem in reconciling the electronic and chemical interpretations of the reduction process. The liberation of hydrogen may be observed during the reduction and after it is complete. It is liberated regularly during the reaction and, in efficient operations, amounts to slightly more than 0.1 cu. ft. per lb. of nitrobenzene reduced. To what extent this hydrogen is generated by the action of water on finely ground cast iron in the presence of iron salts [Eqs. (0) and (7)] or by the hydrolysis of phenylammonium chloride [Eq. (4)] is not known. According to the proponents of the electron theory, such a small amount (about 1 per cent of total requirements) can be attributed to the difficulty in maintaining a practically homogeneous reaction mass. Thus, the liberated hydrogen may be due to the reaction

Eq. (0)] above, because the total iron surface is not in contact with molecules of nitrobenzene. It is rather remarkable, however, that such a high efficiency in proton or hydrogen utilization is obtained in the iron-acid reduction.

Nitrobenzene-iron Ratio.—In works practice, it is customary to use slightly over 2 moles Fe per mole of nitro compound to carry out the reduction process. Under such circumstances, not all the iron is converted to the ferrosoferric oxide, some reducto-active ferrous hydroxide also being present. Iron sludge obtained from the reduction of nitrobenzene gave the analysis shown in Table I. Since magnetic iron oxide consists of 1 part FeO + 1 part Fe_2O_3, if all the iron were converted to the ferrosoferric oxide, the ferric content would be about 66 per cent Fe^{III}.

The following sludge analyses show that slight fluctuations in the ratio or quality of iron will produce magnified differences in its chemical composition.

TABLE I

Expt. No.	Sludge analysis			Iron to Nitrobenzene	
	Metallic iron, %	Ferrous iron, %	Ferric iron, %	Weight ratio	Molar ratio
1	None	11.05	50.16	1:1	2.24:1
2	None	8.44	54.47	1:1	2.24:1
3	1	46.81	13.50	1.1:1	2.45:1

Nitrobenzene, 4,000 lb.; $FeCl_3$, 139 lb.

Industrial experience has shown that it is practicable to operate using a ratio of 2 moles of iron per mole of nitrobenzene as a low limit and 2.5 moles as an upper limit. Undue economy in the use of iron is a faulty practice, as it may lead to side reactions with consequent lowering of the yield.

In works practice, it has been found that when insufficient iron is present, the addition of heat or acid is not effective in carrying the reduction to completion, and a poorly filtering iron oxide sludge is obtained. The introduction of some finely divided iron under such circumstances brings about a vigorous reaction which results in the complete reduction of the nitro compound. Some operators prefer to use very finely divided iron to finish a reduction, and this practice is particularly advisable when the bulk of the iron turnings are not of a good quality.

Chemical Factors in Iron-acid Reduction.—The more important of the physicochemical factors that merit consideration here are the following:

1. Size and physical condition of the iron particles.
2. Homogeneity of the reaction mass.
3. Concentration of the catalyst.
4. Reaction temperature.
5. Heat of reaction.

Physical Condition of Iron.—From a study of the equations outlining the reduction process, it is obvious that the iron fed into the reducer not only supplies the metal adsorption surface but enters into the reactions by providing the iron for the regeneration of the ferrous chloride upon the hydrolysis of the (aniline hydrochloride) phenylammonium chloride and also acts as an oxygen carrier. An analysis of the residual sludge reveals that the bulk of the iron is converted to iron oxides, the degree of oxidation depending on the quantity of iron employed. Experiments have shown that a clean, finely divided, soft, gray cast iron yields the best results. The rate of reduction depends in part on the fineness and porosity of the iron particles, the homogeneity of the charge in the reducer, and the degree of etching imparted to the iron by the preliminary acid treatment. To ensure a thoroughly etched iron and a ready reduction of nitro compound, it is customary to boil the iron-acid suspension before adding any nitro compound. When this precaution is observed, the reaction proceeds very readily, with no danger of a violent deferred reaction.

Size of Particles.—When coarse particles are used, the oxidation of the iron is retarded and an excess of it must be provided. Furthermore, an accumulation of partially oxidized iron, as $Fe(OH)_2$ and $Fe(OH)_3$, oftentimes throws such a load on the stirring mechanism as to bring it to a stop. Since the reaction velocity for nitro compound reduction is a func-

Table II.—Effect of Size of Iron Particles in Reduction of Nitrobenzene
Nitrobenzene, 100 Gm.; Iron, 123 Gm.; Water, 45.5 Cc.; $FeCl_3$ Solution, 7.5 Cc.
(0.035 Gm. Cl as $FeCl_3$ per Cc. of Solution)

Expt. No.	Time, hours	Iron fineness, mesh/sq. cm.	Yield aniline, %
1	1.5	80	100.0
2	7.0	40	96.7
3	9.0	20	78.0
4	2.5	13	66.0
5	9	13	45.6
6	9	20	44.2
7	9	40	78.8
8	2	80	100.2

In experiments 5 to 8, inclusive, 2.90 gm. of *sodium chloride* with 50 cc. of water was used as catalyst. Speed of agitation 34 r.p.m. in all experiments.

tion of the rate of iron oxidation, it is clear that the use of finely divided iron shortens the time of reaction. This fact is brought out in the preceding table from the work of Lyons and Smith;[1] the disparity in results would not however have been so great if a larger quantity of the coarser iron—preferably admixed with some fines—had been used.

Effect of Agitation.—Since the reduction process under consideration is a catalytic reaction, it is clear that the best results are obtainable only when the nitro compound, iron, and water-soluble catalyst are in intimate contact. A stirrer that merely pushes the iron around the bottom of the vessel and permits the charge to separate out into layers does not function efficiently. It is probable, therefore, that a sturdy sleeve-and-propeller or double-impeller type of stirrer will in this case be superior to the slow-moving plow type. Furthermore, most aromatic nitro compounds not containing acidic groups are practically insoluble in faintly acid solution, and thorough mixing is consequently important.

When the rate of reduction is limited by the quantity or quality of the iron used, an increased agitation will not, of course, show a corresponding improvement in operations.

Effect of Concentration of Catalyst.—Theoretical considerations involving the progressive oxidation of the iron indicate the desirability of using 4 to 5 moles of water per mole of nitro compound treated. This approximation is based on the assumption that the iron employed is converted first to ferrous and then to ferric hydroxides as intermediate products during its oxidation to the oxide, thus:

$$2R{\cdot}NO_2 + 4Fe + 8H_2O \rightarrow 2R{\cdot}NH_2 + 4Fe(OH)_3$$
$$2R{\cdot}NO_2 + 5Fe + 11H_2O \rightarrow 2R{\cdot}NH_2 + 5Fe(OH)_3 + 1.5H_2$$

Owing to the fact that part of the iron hydroxides formed lose water to form the ferrosoferric oxide during the course of the reaction, it is entirely possible that the reduction may be made with less than 4 moles of water, provided, however, that a uniform reaction mass can be maintained by effective agitation (see Expt. 10, Table III). Practical problems relating to (1) the agitation of the reaction mass, (2) the promotion of a smooth active reaction, and (3) the conservation of the heat of reduction frequently make it advisable to employ a slight excess over this proportionality. Some reductions require a much larger water ratio, particularly when a mild reaction is required. Unnecessary dilution, however, not only places undesirable restrictions on the productivity of each reducer but also reduces the concentration of the catalyst so that it is less effective.

According to Lyons and Smith, a concentration of 0.035 gm. of Cl per cc. as $FeCl_3$ gives the best results in the preparation of aniline from

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[1] LYONS and SMITH, *Ber.*, **60**, 173 (1927).

TABLE III.—INFLUENCE OF IRON CHLORIDE CONCENTRATION
Nitrobenzene, 100 gm.; 80-mesh Iron, 123 Gm.

Expt. No.	Time, hr.	H_2O, cc.	$FeCl_3$, cc. of solution (0.2315 gm. Cl per cc.)	Gm. Cl as $FeCl_3$ per cc. of solution	Yield $C_6H_5NH_2$ %
1	2	325	50	0.0319	95.4
2	1.5	325	50	0.0319	96.1
3	1.5	151	22	0.0314	93.0
4	2	151	22	0.0314	98.5
5	2	67	11	0.0354	94.1
6	2	16.5	2.5	0.0313	80.0
7	2	33	2.5	0.0165	88.0
8	2	33	3	0.0197	90.0
9	2	47.5	4	0.0184	95.0
10	1.5	45.5	7.5	0.035	100.0

nitrobenzene.[1] From the data (Table III), it can be seen that no benefit were derived from the use of a larger quantity of ferric chloride. As is t be expected, the important factor is the concentration of the catalyst It is interesting to observe that the Cl^- content is only about 1 per cen of the amount theoretically required by the equation

$$C_6H_5NO_2 + 3Fe + 6HCl \rightarrow C_6H_5NH_2 + 3FeCl_2 + 2H_2O$$

When nonjacketed reducers are used and considerable water as liv steam is introduced, it is clear that the concentration of the water-solubl

TABLE IV.—COMPARATIVE ACTIVITY OF $FeCl_3$ AND NaCl, IN THE REDUCTION O NITROBENZENE[1]
Nitrobenzene, 100 Gm.; Iron, 123 Gm.; r.p.m., 34

Expt. No.	Time, hours	Iron fineness through mesh	Chloride used	H_2O, cc.	Total chloride	Cl per cc. solution, gm.	Yield $C_6H_5NH_2$, %
1	2	80	NaCl	50	1.523 gm.	0.0183	88.0
2	2	80	$FeCl_3$	47.5	4.0 cc.	0.0184	95.0
3	2	80	NaCl	50	2.90 gm.	0.035	100.2
4	1.5	80	$FeCl_3$	45.5	7.5 cc.	0.035	100.0
5	7	40	$FeCl_3$	45.5	7.5 cc.	0.035	96.7
6	9	20	$FeCl_3$	45.5	7.5 cc.	0.035	78.0
7	9	13	NaCl	50	2.90 gm.	0.035	45.6
8	9	40	NaCl	50	2.90 gm.	0.035	78.8
9	9	20	NaCl	50	2.90 gm.	0.035	43.0

[1] Lyons and Smith conclude from these results that sodium chloride is about 84 per cent as efficient as ferric chloride.

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[1] LYONS and SMITH, *loc. cit.*

atalyst is continuously being lowered and, consequently, it becomes less ffective. Furthermore, with increasing volume, it becomes more dificult to maintain a homogeneous reaction mass. It is obvious that he reaction velocity cannot be at a maximum when the iron, wateroluble catalyst, and nitro compound are not thoroughly mixed.

Ferric chloride reacts more actively than sodium chloride in the atalytic iron-salt reduction of nitro compounds. The comparative lata relating to the preparation of aniline are given in Table IV.

Reaction Temperature.—It has been found that the use of a high atalyst concentration (3 or more per cent compared to nitrobenzene taken) during reduction results in a finely divided iron sludge of probable commercial value. This result can be obtained by limiting the quantity of water introduced into the jacketed reducer and utilizing the heat of reaction to carry on the reaction. An obvious advantage arising from operating with such concentrated solutions is the fact that the charge is easily maintained at the boiling temperature. The vigorous reflux that characterizes such a reduction ensures against the formation of intermediate products of reaction. The reaction is not only rapid and efficient but economical on account of the lower consumption of steam.

Heat of Reaction.—A study of the thermal factors relating to the reduction of nitrobenzene shows that the reaction is distinctly exothermic. It is necessary, therefore, to remove the surplus heat generated while maintaining the reduction at the optimum reaction temperature. When nonvolatile materials are treated, as in the conversion of *p*-nitroaniline to *p*-phenylenediamine, flumes of suitable diameter and height are sufficient. When volatile nitro compounds are used, an efficient condenser—preferably one in which the vapors pass downward over vertical water-cooled coils—gives eminently satisfactory results.

The data below show the heat in B.t.u. generated during the "feed" and reduction of a 1,200 lb. charge of nitrobenzene.

Operation	Heat Generated, B.t.u.
Feed	1,805,000
Reduction	488,000
Total heat liberated	2,293,000
Heat of conversion per pound nitrobenzene	1,911

Ferrous Sulfate as Catalyst.—It has long been known that sulfuric acid could be substituted for hydrochloric acid in the reduction process. As a rule, the amino compounds obtained from its use, particularly in the case of solid products, are darker and the yields lower. These disadvantages appear to be diminished when the sulfuric acid is introduced as sodium acid sulfate. When this is used alone or preferably in conjunction with a calculated quantity of sodium chloride, a very economical and satisfactory promotor is obtained. The acid sulfate ($NaHSO_4$) may be considered as having 40.8 per cent available H_2SO_4; but as a rule, the niter cake of commerce averages about 31 per cent acidity. When it is used in conjunction with sodium chloride, Davis claims it to be an excellent promotor of the catalytic action.[1] This is apparently due to the formation of hydrochloric acid at the start of the process and the formation of ferrous chloride as a secondary reaction. Davis suggests the use of 2 lb. of H_2SO_4 as 6 lb. of niter cake per 100 lb. of nitrobenzene. When the niter cake is employed in conjunction with sodium chloride, sufficient NaCl must be added to use up the acidity. Thus, 2.4 lb. of sodium chloride with 6 lb. of niter cake per 100 lb. of nitro compound give satisfactory results. The niter cake is first ground then added, along with the sodium chloride to the water, and finely divided iron in the reducer.

Recovery of the Catalyst.—In the technical preparation of amines by catalytic reduction with iron and a soluble salt, it is not customary to recover and utilize the dissolved catalyst. This step is not always feasible, particularly when the amino compound is also soluble in aqueous solutions. In many instances, however, such a step could be made part of the chemical engineering operations employed in separating the amine from the aqueous suspension of iron compounds. Utilization of the aqueous portion in subsequent reductions appears to be an excellent method of introducing the catalyst in an active form. In this connection, it is known that the impure mother liquors from the aniline hydrochloride crystallizing pans can be used advantageously.

IV. TIN AND HYDROCHLORIC ACID REDUCTION

The reduction of aromatic nitro compounds with tin and hydrochloric acid may be represented by the following equation:

$$2R{\cdot}NO_2 + 3Sn + 12HCl \rightarrow 2R{\cdot}NH_2 + 3SnCl_4 + 4H_2O$$

Owing to the comparatively high cost of tin, this method of effecting reductions has not achieved significant commercial importance. In place of tin and hydrochloric acid, a solution of stannous chloride in hydrochloric acid can be employed; but there is little advantage, in general, in this procedure, as double the amount of tin must be used to effect the reduction.

There are, however, occasional uses for stannous chloride reductions on account of the mildness of the reaction. It can be employed in the reduction of 4, 4′-dinitrodiphenylamine which accompanies *p*-nitroaniline as an impurity when the latter is prepared by the ammonolysis of *p*-nitrochlorobenzene. Stannous chloride is also employed when it is desired to reduce one nitro group of two originally present. In alcoholic solution, this reduction proceeds very smoothly, yielding excellent products.

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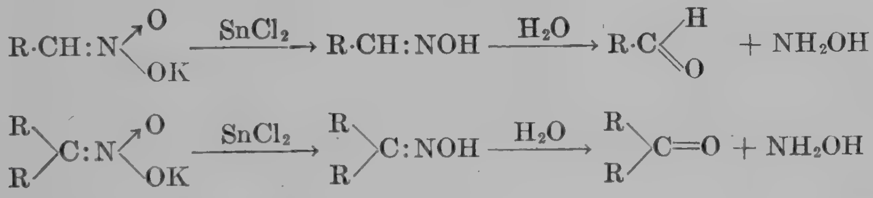
[1] Davis, U. S. 1,663,473 (1928).

Stannous chloride in hydrochloric acid can also be employed for the reductions of the nitroparaffins. Ordinarily, however, this procedure results in the formation of the related hydroxylamine in addition to the primary alkylamine:

$$R\cdot CH_2NO_2 \xrightarrow{2H_2} R\cdot CH_2NHOH \xrightarrow{H_2} R\cdot CH_2NH_2$$

When, however, a large excess of stannous chloride and fuming hydrochloric acid are used, primary and secondary nitro compounds are reduced to the corresponding oximes. Thus, by adding an aqueous solution of the alkali salt of the acinitro compound to about 2.5 times the theoretical quantity of $SnCl_2$—HCl, as required by the equations below, the oxime is formed.



$$R\cdot CH{:}N\genfrac{}{}{0pt}{}{\nearrow O}{\diagdown OK} \xrightarrow{SnCl_2} R\cdot CH{:}NOH \xrightarrow{H_2O} R\cdot C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown\!\!\diagdown O} + NH_2OH$$

$$\genfrac{}{}{0pt}{}{R\diagdown}{R\diagup}C{:}N\genfrac{}{}{0pt}{}{\nearrow O}{\diagdown OK} \xrightarrow{SnCl_2} \genfrac{}{}{0pt}{}{R\diagdown}{R\diagup}C{:}NOH \xrightarrow{H_2O} \genfrac{}{}{0pt}{}{R\diagdown}{R\diagup}C{=}O + NH_2OH$$

If the charge is neutralized and live steam introduced, the oxime will be distilled over. When steam is passed into the acid charge, however, hydrolysis occurs with the formation of a ketone or aldehyde and hydroxylamine. The carbonyl compound will distill over, whereas the hydroxylamine hydrochloride remains in solution.

Stannous Chloride as a Reducing (and Chlorinating) Agent.—Under anhydrous conditions in the presence of acetic acid, stannous chloride may be used for the reduction of aromatic nitro compounds, acetylating the base and in many cases chlorinating the resultant anilide *in situ.*[1] The concomitant reduction and chlorinating of nitrobenzene may be indicated as follows:

$$C_6H_5\cdot NO_2 \rightarrow C_6H_5\cdot NH_2 \rightarrow C_6H_5\cdot NH\cdot COCH_3 \rightarrow C_6H_4Cl\cdot NH\cdot COCH_3$$

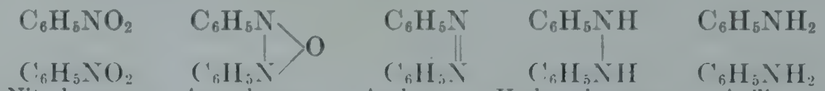
Generally, monochlorination takes place in the para position to the original nitro group. In para substituted nitro compounds, no chlorination takes place except in the case of *p*-chloronitrobenzene, which, only if hydrogen chloride is present during the reduction, gives 2, 4-dichloroacetanilide; in the absence of hydrogen chloride, the product is *p*-chloroacetanilide.

[1] Kiewiet and Stephen, *J. Chem. Soc.*, **1931,** 82.

V$_A$. REDUCTION WITH ZINC OR IRON IN STRONG ALKALINE SOLUTION

When nitrobenzene or its homologues are treated in alkaline solution in the presence of finely divided zinc or iron, they can be reduced step by step to the hydrazo stage. Such hydrazo compounds—hydrazobenzene, hydrazotoluene, hydrazoanisole—may be converted readily to benzidine, tolidine, and dianisidine by intramolecular rearrangement in cold concentrated hydrochloric acid.

The several steps in the reduction of nitrobenzene are represented by the following graphic formulas:



$$\begin{matrix} C_6H_5NO_2 & C_6H_5N \\ & | \quad \rangle O \\ C_6H_5NO_2 & C_6H_5N \end{matrix} \qquad \begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix} \qquad \begin{matrix} C_6H_5NH \\ | \\ C_6H_5NH \end{matrix} \qquad \begin{matrix} C_6H_5NH_2 \\ \\ C_6H_5NH_2 \end{matrix}$$

Nitrobenzene Azoxybenzene Azobenzene Hydrazobenzene Aniline

Ethanol and methanol are usually employed in the zinc-alkali reduction in order to moderate the reducing activity of the system which tends toward the production of some aniline in the final stages. The use of zinc in alcoholic caustic soda, which was the first procedure for the technical preparation of hydrazobenzene, has to a considerable extent been replaced by iron in alkaline solution. Although the materials involved in the former process are more costly, the method is still employed on account of the comparative simplicity of the operation. Numerous modifications have, however, been made so that the residual zinc, alkali, and alcohol are recovered. This improved technic is described later in this chapter under technical operation.

When zinc is employed, some of it is dissolved in the alkaline solution with the evolution of hydrogen, the zinc hydroxide first formed dissolving in the excess of alkali:

$$Zn + 2\overset{+}{H} + 2O\overset{-}{H} \rightarrow \overset{++}{Zn} + 2O\overset{-}{H} + H_2\uparrow \rightarrow Zn(OH)_2$$
$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$$

Zinc hydroxide is weakly basic and gives salts with acids; but with respect to strong bases, it is weakly acidic. Zinc hydroxide is very soluble in an excess of alkali, zinc oxide acting as an acid-forming oxide toward the strong alkalies, and it is upon this fact that the solution of zinc in alkalies with evolution of hydrogen depends. Freshly precipitated zinc hydroxide requires nearly seven molecular proportions of caustic soda in concentrated solution to dissolve it completely, and the solution thus formed is not permanent, zinc hydroxide being gradually precipitated from it in a less soluble form. Only a very small amount of sodium zincate is ever present in solution, the greater part of the dissolved hydroxide being probably present in the colloidal state.[1] The equilibrium may be expressed by the following equation, zinc hydroxide (or hydrous zinc oxide) being represented as a weak acid H_2ZnO_2:

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[1] GOUDRIAAN, *Proc. Acad. Sci. Amsterdam*, **22**, 179 (1919).

$$H_2ZnO_2 + 2NaOH \rightleftarrows Na_2ZnO_2 + 2HOH$$

The reduction of the nitro compound to the hydrazo stage may be represented by the following equation:

$$10NaOH + 5Zn + 2R\cdot NO_2 \rightarrow R\cdot\underset{H}{\dot{N}}\cdot\underset{H}{\dot{N}}\cdot R + 5Na_2ZnO_2 + 4H_2O$$

In technical operations, an excess of 15 to 50 per cent zinc (based on the preceding equation) is used. The quantity of alkali employed is, however, only about 2 to 3 per cent of the theoretical. Here, as in the case of acid reductions, there is a hydrolysis of the intermediate soluble catalytic agent which the presence of metals encourages. In this process, the sodium zincate is hydrolyzed with the regeneration of sodium hydroxide, the zinc hydroxide being ultimately converted to the oxide:

$$Na_2ZnO_2 + 2H_2O \overset{Zn}{\rightleftarrows} Zn(OH)_2 + 2NaOH$$

In spite of the fact that the atomic weight of iron is less than that of zinc and that iron furthermore can be oxidized to Fe_2O_3, the excess of ordinary iron that must be actually employed in this reduction (when it replaces zinc) is very much greater. This circumstance is attributed to the lower activity of iron. It is necessary, therefore, to facilitate the catalytic and hydrolytic reactions by employing a fine quality of iron, which gives a maximum surface and is free from oil. In works practice, it is expedient to etch the iron before using, by treating it with a strong alkali solution, whereupon the metal assumes the appearance of damp sand. Dreyfus has found that the ratio of both iron and alkali with respect to nitrobenzene can be substantially lowered by using iron that has been prepared by the reduction of the oxides.[1] Such iron is obtained in a very finely divided condition and has an extended active surface with respect to its mass. Compared with alkali-etched iron turnings, only about 65 to 75 per cent of the quantity need be used; the molar ratio of nitrobenzene to iron and alkali, respectively, here being approximately 2:4:8. This indicates that the oxidation of the iron will occur closely as follows:

$$4Fe + 10H_2O \rightarrow 2Fe(OH)_2 + 2Fe(OH)_3 + 5H_2$$

The iron-alkali reduction, like the zinc-alkali process, is subject to numerous modifications. The following example illustrates the procedure in carrying out such reductions:[1]

Progressive Reduction of Nitrobenzene to Hydrazobenzene.—*a.* Fifty parts of finely divided iron, obtained by reducing iron oxide with hydrogen or by the thermal decomposition of iron carbonyl, is added to 100 parts of nitrobenzene contained in a reducer fitted with an efficient stirrer. The suspension is heated to 90°C., and 80 parts of 60 per cent sodium hydroxide is gradually added. The mixture is then stirred at 100°C., the temperature being maintained by supplying steam or cooling water to the jacket of the reducer. The course of the reaction may be observed by the change of color and the disappearance of the odor of nitrobenzene. A more exact indication may be obtained by determining the setting point on a sample of the charge (Fig. 2), since this changes with each phase of the reaction. As the reduction proceeds, the setting point drops from about 5° (corresponding to nitrobenzene) to a minimum of −13°C., at which time about 40 per cent of the nitro compound is converted to azoxybenzene. The setting point then gradually rises to 31°C., at which time the odor of nitrobenzene has disappeared and the azoxy compound can be discharged.

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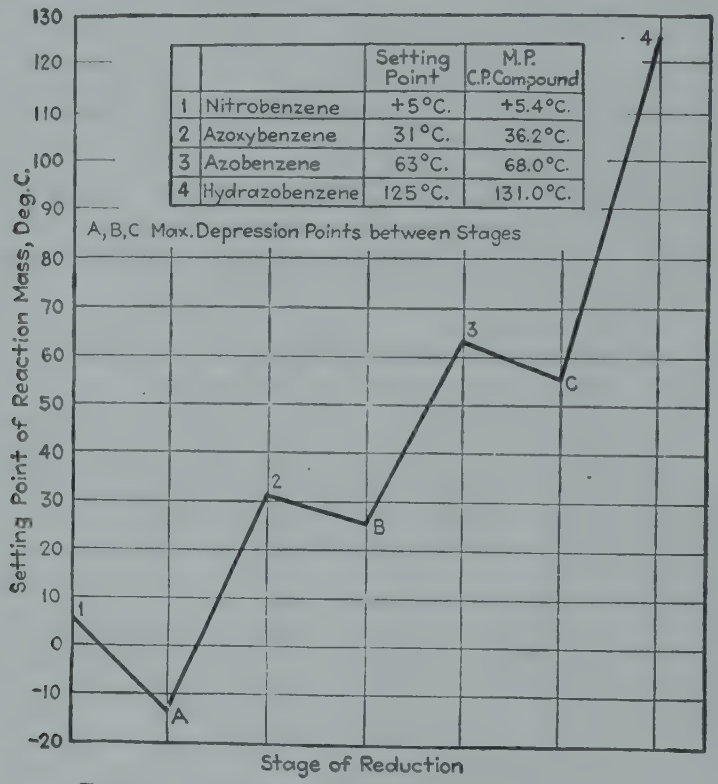
[1] Dreyfus, U. S. 2,010,067 (1935).



		Setting Point	M.P. C.P. Compound
1	Nitrobenzene	+5°C.	+5.4°C.
2	Azoxybenzene	31°C.	36.2°C.
3	Azobenzene	63°C.	68.0°C.
4	Hydrazobenzene	125°C.	131.0°C.

FIG. 2.—Alkali-iron reduction of nitrobenzene.

b. Azobenzene can be obtained upon further reduction of the azoxy compound by adding a paste consisting of 16 parts iron and 40 parts of 60 per cent caustic soda and heating at 110 to 120°C. The setting point of the reduction mass first sinks to a minimum of 25°C. and then rises to about 63°C. The apparatus may then be stopped and the azobenzene discharged.

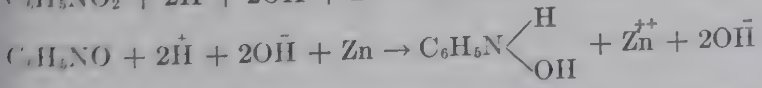
c. In order to proceed to the next stage of reduction, *i.e.*, to hydrazobenzene, it is necessary again to add a paste consisting of 16 parts iron and 40 parts of 60 per cent caustic soda solution. The setting point of the mass sinks to a minimum of 55°C. and then rises to 122 to 125°C. In order to prevent the reduction mass from solidifying, it is necessary either to raise the temperature to 130°C. or to add a solvent *e.g.*, benzene, to the reaction mixture. The introduction of benzene in sufficient quantities also affords a convenient means of separating and decanting the hydrazobenzene from the iron-alkali residues.

It is difficult to remove the hydrazobenzene from the iron sludge at this point, and a number of modifications of this process have consequently been advocated. A practical suggestion involves the removal of azobenzene and reducing this compound by zinc in alcoholic alkaline solution at 60°C. The reduction mass is filtered, and the zinc residues are boiled up with fresh alcohol. The filtrate separates into two layers, of which the lower contains aqueous sodium zincate and the upper is an alcoholic solution of hydrazobenzene. The alcoholic layer is separated and saturated with carbon dioxide to precipitate the alkali. After filtering, the alcoholic solution is evaporated to obtain the hydrazobenzene, for which Fierz claims practically quantitative yields.[1]

V$_B$. REDUCTION WITH ZINC IN WEAKLY ALKALINE SOLUTIONS

In the preceding pages, it was shown that the mechanism of reduction with zinc and strongly alkaline solutions led to the formation of azoxybenzene as the first step in the reduction of nitrobenzene. Brand and his coworkers have shown that when faintly alkaline systems are employed, the principal initial product of reduction is β-phenylhydroxylamine. The systems—zinc + calcium chloride and zinc + ammonium chloride—are not neutral but quite alkaline to phenolphthalein. When the hydrogen electrode and indicators were employed, it was found that in the preparation of β-phenylhydroxylamine from nitrobenzene by means of zinc dust and aqueous calcium chloride, the reduction liquid has a pH between 10.5 and 11.7, which corresponds to the alkalinity of 0.01 *N* alkali. When NH_4Cl was substituted for $CaCl_2$ in the reducing system, the pH was between 8 and 9. Brand and Modersohn advanced the following scheme in the reduction of nitrobenzene to phenylhydroxylamine:[2]

$$C_6H_5NO_2 + 2\overset{+}{H} + 2O\overset{-}{H} + Zn \rightarrow C_6H_5NO + H_2O + \overset{++}{Zn} + 2O\overset{-}{H} \qquad (a)$$



$$C_6H_5NO + 2\overset{+}{H} + 2O\overset{-}{H} + Zn \rightarrow C_6H_5N\begin{matrix}\diagup H\\ \diagdown OH\end{matrix} + \overset{++}{Zn} + 2O\overset{-}{H} \qquad (b)$$

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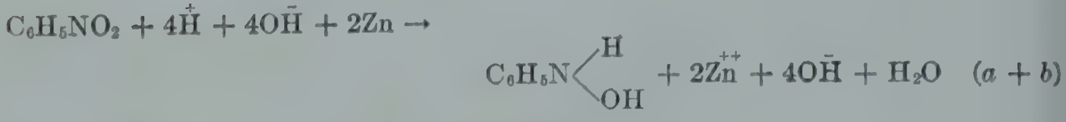
[1] FIERZ-DAVID, "Dye Chemistry," D. Van Nostrand Company, Inc., 1921 (trans.).

[2] BRAND and MODERSOHN, *J. prakt. Chem.*, **120**, 160 (1928).



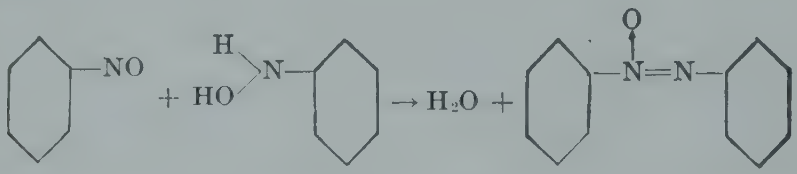
$$C_6H_5NO_2 + 4\overset{+}{H} + 4O\overset{-}{H} + 2Zn \rightarrow C_6H_5N\begin{matrix}H\\OH\end{matrix} + 2\overset{++}{Zn} + 4O\overset{-}{H} + H_2O \quad (a + b)$$

$$2\overset{++}{Zn} + 4O\overset{-}{H} \rightleftarrows 2Zn(OH)_2$$

Zinc and ammonium chloride can also be used advantageously for the reduction of nitroparaffins to alkylhydroxylamines:

$$CH_3{\cdot}NO_2 \xrightarrow{Zn + NH_4Cl} CH_3NHOH$$

Brand and Mahr showed that the formation of azoxybenzene in the reduction of nitrobenzene is brought about by the condensation of nitrosobenzene and phenylhydroxylamine, the latter being intermediate products of reduction.[1]



VI. REDUCTION OF NITRO COMPOUNDS WITH ALKALI OR METAL SULFIDES

Alkaline reductions are milder than the iron-acid reductions; and for this reason, modifications of this process find extensive use in technical operations. By utilizing alkali or metal sulfides, it is possible to control better the rate and degree of reduction. Although ammonium sulfide is sometimes used, sodium sulfide or sodium disulfide are most frequently employed. The sulfides of iron and manganese have also been found of value in reduction processes but thus far have not found widespread industrial applications.[2]

The more important uses of alkali or metal sulfides are (1) preparation of nitroamines from dinitro compounds; (2) reduction of nitrophenols;[3] (3) reduction of aromatic nitro compounds containing a halogen substituent; (4) preparation of aminoazo compounds from the corresponding nitro derivatives. Illustrative examples of reductions with alkali and metal sulfides are given in the technical section.

Sulfides in the Reduction Process.—Despite its low heat of formation, hydrogen sulfide is very stable.

$$H_2 + S \text{ gas} \rightarrow H_2S + 4.82 \text{ cal.}$$

At 400°, dissociation of the gas begins, and it is complete at 1700°C.

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[1] Brand and Mahr, *J. prakt. Chem.*, **131**, 119 (1931).

[2] Dawes, U. S., 1,765,660 (1930).

[3] See Astle and Cropper, *J. Am. Chem. Soc.*, **65**, 2395 (1943), for mechanism of reaction.

Its activity apparently depends on the fact that here sulfur has a valence of -2 and consequently enters readily into reactions involving oxidation and reduction. The gas is useful, therefore, as an active reducing agent. Even at room temperature, hydrogen sulfide reduces sulfur dioxide with the precipitation of sulfur.

The activity of alkali sulfides in the reduction of nitro compounds is due to the ease with which the former take up oxygen.

$$4R{\cdot}NO_2 + 6Na_2S + 7H_2O \rightarrow 4R{\cdot}NH_2 + 3Na_2S_2O_3 + 6NaOH \qquad (1)$$

$$R{\cdot}NO_2 + Na_2S_2 + H_2O \rightarrow R{\cdot}NH_2 + Na_2S_2O_3 \qquad (2)$$

At one time, an appreciable proportion of the aniline production was made according to Eq. (2). This process runs very satisfactorily and is devoid of problems relating to the separation and disposal of iron sludge.[1] It would, indeed, be a very attractive procedure if a profitable use or outlet were found for the by-product sodium thiosulfate to offset the comparatively higher cost of the sulfide reducing agent.

Concentration of Sulfide.—Whereas some agreement appears to exist regarding the optimum concentration of the catalyst in acid reductions, there seems to be no such condition for alkali sulfide reductions. This situation is, of course, brought about by the fact that most alkaline reductions are employed when only a limited reduction is desired. Conditions in the reduction system must consequently be adjusted with respect to each type of nitro compound and the degree of reduction required. In the reduction of *m*-dinitrobenzene to *m*-nitroaniline, there is considerable variation in the type and concentration of the alkaline reducing agent. Thus, in the reduction of 100 parts of *m*-dinitrobenzene, the conditions shown below have been recommended.

REDUCTION OF *m*-DINITROBENZENE

H_2O, parts	Reducing agent, parts	S/H_2O, %	$S/R{\cdot}NO_2$, %	Authority
880	Na_2S, 62	2.7	23.8	Fierz, Farbenchemie
2,300	Na_2S, 25 S, 20	1.5	35.0	Cobenzl, *Chem. Ztg.*, **37, 1913**
1,200	MnS, 105	3.2	38.7	Dawes, U.S. 1,765,660

VII. FERROUS SULFATE IN ALKALINE SOLUTION AS A REDUCING AGENT[2]

Although ferrous sulfate in alkaline solutions acts as a strong reducing agent, the system has only a limited usefulness in the commercial reduction of nitro compounds. The amount of ferrous sulfate used is slightly in excess of that required by theory, which is 6 moles of ferrous sulfate to 1 mole of the nitro compound.

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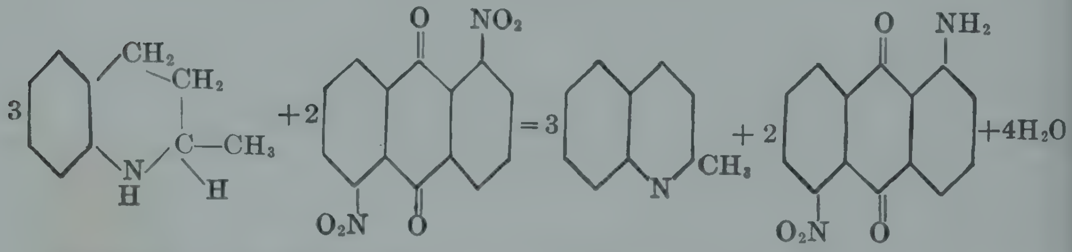
[1] Ger. 144,809 (1902).

[2] U.S. 1,765,660 (1930).

$$R{\cdot}NO_2 + 6FeSO_4 + H_2O \rightarrow R{\cdot}NH_2 + 2Fe_2(SO_4)_3 + Fe_2O_3$$

m-Nitrobenzaldehyde can be converted to the amino compound utilizing this procedure by putting it into solution as a bisulfite compound with double its weight of a 30 per cent solution of sodium bisulfite. This solution is slowly delivered to a vat containing the required quantity of ferrous sulfate in 3 parts of water and to which one-third of its weight of calcium carbonate has been added. The mixture is boiled with stirring. Carbon dioxide is given off with effervescence, and reduction takes place rapidly. The amino compound can be extracted from the solution after first acidifying with hydrochloric acid to expel the sulfur dioxide.

VIII. REDUCTION OF NITRO COMPOUNDS WITH HYDROGENATED QUINOLINE BASES



Berthold has shown that nitroanthraquinones and their nuclear substituted products can be reduced by means of hydrogenated bases of the quinoline series.[1] When 1, 2, 3, 4-tetrahydro-2-methylquinoline is employed, the reduction runs smoothly. The reduction can be made to take place in the presence of diluent solvents such as *o*-dichlorobenzene, pyridine, glacial acetic acid, or, preferably, 2-methylquinoline. The reaction proceeds at moderate temperatures without catalysts; and when 2-methylquinoline is employed as the diluent, the mixture of the latter and the unoxidized hydromethylquinoline can again be catalytically hydrogenated. The regenerated hydrogenated quinoline base is again used in the process. It is apparent, therefore, that hydrogen is the real reducing agent whereas the base acts as a carrier only.

IX. SODIUM HYPOSULFITE IN ALKALINE SOLUTIONS AS A REDUCING AGENT

Sodium hyposulfite ($Na_2S_2O_4$) in alkaline solutions has come to play an important part in the reduction of anthraquinone and indigoid derivatives to the leuco compounds. Although it is an active reducing agent, it finds only a limited use in the reduction of nitro compounds because of the comparatively greater cost attached to its use.

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[1] Berthold, U. S. 1,691,428 (1928).

Sodium hyposulfite can be used as the white crystalline product of commerce, or it can be prepared in the course of the reaction by adding zinc dust to a solution of sodium acid sulfite. The latter procedure is employed by Rogers for the reduction of indigo, and by Sidgwick and Callow for the preparation of *o*-aminophenol from the corresponding nitro derivative.[1,2] The reaction involved is as follows:

$$2NaHSO_3 + SO_2 + Zn \rightarrow Na_2S_2O_4 + ZnSO_3 + H_2O$$

The required SO_2 is obtained by the introduction of a mineral acid to the reaction mixture during reduction.

According to Sidgwick and Callow, aminophenol is prepared by mixing *o*-nitrophenol with 4.5 molecular proportions of sodium bisulfite as a 25 per cent solution. The charge is warmed, and zinc dust added at such a rate that the liquid keeps boiling. Completion of the reaction is indicated by the disappearance of the yellow color when spotting on filter paper. The *o*-aminophenol is obtained by filtering the hot solution and permitting the filtrate to cool, whereupon the amino compound crystallizes out.

X. USE OF PARAFFINS AND CYCLOPARAFFINS AS REDUCING AGENTS

A variety of paraffinic and cycloparaffinic hydrocarbons such as methane, ethane, pentane, cyclohexane, and natural gas can be used in conjunction with base metal hydrogenation catalysts for the reduction of nitro compounds.[3] The reaction has been found to be applicable to the reduction of nitrobenzene, nitrotoluenes, nitroxylenes, nitropropane, etc. The per-pass conversions are in general not high. Yields of 30 to 55 per cent have been obtained in the reduction of nitrobenzene with the use of cyclohexanol and methane, respectively. Accompanying the aniline are found unconverted nitrobenzene and the end products of hydrocarbon oxidation—carbon dioxide and a trace of carbon monoxide.

The catalysts may vary somewhat in composition, but they must be capable of catalyzing the pyrolyses of the hydrocarbons as well as the reduction of the nitro compounds to amines. The ferrous metal chromites modified by the addition of cadmium chromite and nickel or cobalt salts—supported or unsupported—are useful catalysts.

Reductions by paraffins can be carried out in either the liquid phase or the vapor phase and are best effected in a temperature range of 350 to 425°. The reaction is strongly exothermic; and, in vapor-phase operations, provision must be made for the dissipation of the heat (1) by diluting the reaction mixture with inert gases or using a large excess of

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[1] Rogers, U. S. 1,721,319 (1929).

[2] Sidgwick and Callow, *J. Chem. Soc.*, **125**, 2452 (1924).

[3] Castner and Lawson, U. S. 2,377,071 (1945).

hydrocarbon, (2) by placing the catalyst in metal tubes of small diameter (½ in.) so that the excess heat may be rapidly transferred to a constant-temperature bath surrounding the catalyst-containing tubes, and (3) by controlling the rate at which the reaction mixture is brought into contact with the catalyst.

The direct use of paraffins or natural gas appears to provide an inexpensive method for introducing amino compounds—which are valuable blending agents for gasoline—into aviation fuels. It may prove more advantageous, however, to use by-product refinery hydrogen or carbon monoxide-hydrogen mixtures prepared in an integrated plant (see next section).

XI. REDUCTION BY HYDROGEN WITH THE AID OF A CATALYST

Developments in the production of hydrogen-containing gases from natural gas (principally methane), particularly in conjunction with the wartime production of ammonia, are destined markedly to affect the actual as well as the geographic production of amino compounds, not only in the United States but throughout the world. In the production of ammonia, the water gas ($H_2 + CO$) can be obtained by the interaction of coke or natural gas and steam. The mixture $3H_2 + N_2$ can be prepared by appropriate blending of water and producer gases (after removal of carbon oxides) or by using methane to burn the oxygen from air to make nitrogen which is mixed with the hydrogen obtained from the methane-steam reactions.

During the war period, the price of ammonia in tanks was reduced to about 3 cts. per pound, and the cost of producing nitric acid therefrom was diminished accordingly. Thus, the cost of producing nitro compounds and effecting their reduction by hydrogen-containing gases has been appreciably lowered. See chapter on Hydrogenation for a more detailed discussion of hydrogen production and hydrogenation processes.

The reduction of nitro compounds with hydrogen or hydrogen-containing gases can be carried out in either the liquid or the vapor phase. Furthermore, aminations brought about by gaseous hydrogen in the presence of a catalyst can be carried out in a continuous manner; and when the amino compound is readily susceptible to purification by physical means, such processes are economical and attractive. Brief descriptive examples of each of these methods are given below.

Nord has shown that the reduction of nitrobenzene by hydrogen gas in the presence of colloidal platinum gives rise to the same intermediate compounds that are obtained by electrolytic reduction or by reduction with metals in acid or neutral solutions.[1] The following shows the course of the reaction:

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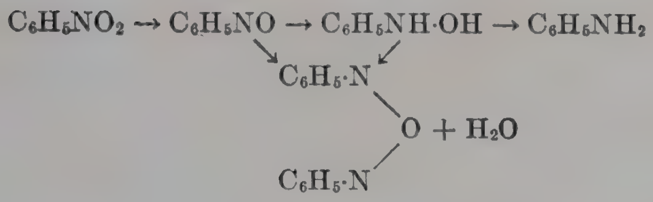
[1] Nord, *Ber.*, **52**, 1705 (1919).



$$C_6H_5NO_2 \rightarrow C_6H_5NO \rightarrow C_6H_5NH{\cdot}OH \rightarrow C_6H_5NH_2$$

$$\begin{array}{l} C_6H_5{\cdot}N \\ \qquad\quad O + H_2O \\ C_6H_5{\cdot}N \end{array}$$

Liquid-phase Reductions

Hydrogen in the Presence of Iron.—According to Von Girsewald, nitrobenzene and water are charged into an autoclave containing finely divided iron, and a pressure of 30 atmos. carbon dioxide and 60 atmos. hydrogen is applied.[1] The reduction is carried out at 300 to 350°C., at which temperature a rapid absorption of hydrogen occurs.

Herold and Koppe show that milder temperature conditions can be used in liquid-phase reductions with hydrogen in the presence of iron if a spongy iron containing natural or added sulfur is used.[2] Small quantities of sulfur or ammonium sulfide may be added to the reaction system to accelerate the reduction.

Reduction with Hydrogen in Alkaline Sulfide Solution.—It is not necessary to employ the calculated quantity of sulfide when an alkaline reduction is carried out under pressure in the presence of hydrogen. It has been found that, by means of readily soluble sulfides, the reaction can be carried out under hydrogen or water-gas pressure and at an elevated temperature using only one-twentieth to one-sixtieth of the quantity of sulfide required in the absence of reducing gases.[3] Under such circumstances, the small sulfide concentration is sufficient to effect complete reduction of the nitro compound, inasmuch as the polysulfide or thiosulfate formed is continuously reduced again to the sulfide by the action of the hydrogen. The sulfide solution is therefore able to convert any desired quantity of the nitro compound to the amino derivative.

Solutions of polysulfides and thiosulfates may also be used. It has been found that in this reaction the whole of the thiosulfate is not continuously reduced to sulfide by hydrogen, a small portion being converted to sulfate. Under the conditions used in this operation, *viz.*, 150°C., under a pressure of 100 atmos. of hydrogen, the sulfate cannot be reduced by hydrogen. The regenerated sulfide is, however, the active catalytic agent.

Reduction with Hydrogen in Strong Acid Solutions.—When nitro compounds are suspended in sulfuric acid and treated with hydrogen in the presence of sulfides of molybdenum, cobalt, tungsten, or platinum, aminophenols are obtained.[4] In all probability, the mechanism of reac-

[1] Girsewald, Ger. 281,100 (1914).

[2] Herold and Koppe, U. S. 1,854,258 (1932).

[3] U. S. 1,662,421 (1928).

[4] Henke and Vaughen, U. S. 2,198,249 (1940).

tion proceeds via the formation of a hydroxylamine, which undergoes immediate rearrangement to an aminophenol. The reaction for nitrobenzene may be represented thus:

$$C_6H_5NO_2 \xrightarrow[MoS_3]{H_2} C_6H_5NHOH \xrightarrow{H_2SO_4} 1,\ 4\text{-}HOC_6H_4NH_2$$

The reduction is carried out at about 150°, with the use of a hydrogen pressure of 400 to 500 lb. The degree of aminophenol production depends largely on the composition of the catalyst as can be seen from the data in Table V.

TABLE V.—HYDROGENATION OF NITROBENZENE IN H_2SO_4 SOLUTION

Materials	Parts by weight			
Nitrobenzene	369	369	369	369
Sulfuric acid	300	600	300	300
Water	450	900	450	450
Catalyst	10 MoS_3	10 MoS_3	10 CrS_3	10 CoS
Aniline[1]	100	225	76	189
p-Aminophenol	175	10	181	30
Total amines	275	230	257	219

[1] Theoretical yield of aniline, 279 parts.

Hydrogen in the Presence of Platinum Oxide.—*Amino derivatives having enolizable groups* have a tendency to react with themselves and may also be attacked at the enol grouping unless mild reducing conditions are employed. The reduction of nitro compounds, such as *m*-nitroacetanilide which contains an enolizable group, can be satisfactorily carried out by first dissolving the compound in dilute aqueous alkali and subsequently treating it with hydrogen at 35 lb. pressure in the presence of a platinum oxide catalyst. A concentration of aqueous alkali of about one-fifth normal (0.8 per cent) and a reaction temperature of 20° give satisfactory results.[1]

Hydrogen in the Presence of Metal Sulfides.—Owen has shown that catalysts consisting of metal sulfides of molybdenum, zinc, and magnesium, or of copper sulfide supported on alumina can be used in converting aromatic nitro compounds to amines.[2] Thus when a liquid feed consisting of 28 per cent nitroxylenes and 72 per cent by weight "alkylate" fuel (or xylene, cyclohexane, etc.) is heated at 220 to 250°, under 2,500 lb. hydrogen pressure in an autoclave, xylidines are obtained. Aromatic amines such as aniline, xylidines, and cumidine form excellent knock suppressors when added to aviation fuel.

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[1] Kenyon and Lowe, U. S. 2,311,054 (1943).

[2] OWEN, U.S. 2,402,439; 2,402,440 (1946).

VAPOR-PHASE REDUCTION

A large number of patents have been issued covering the vapor-phase reduction of nitrobenzene by hydrogen-containing gases in the presence of metal catalysts.[1] Such a process has many attractive features. Some of these are (1) continuous conversion of reactants to finished amine, (2) minimum operating labor requirements, (3) low steam and power costs by utilizing the heat in vapors leaving the catalytic chamber, and (4) absence of industrial waste problems, *e.g.*, disposal of iron oxide sludge. Such a process is particularly suited for works such as an ammonia synthesis plant that have a water-gas plant, and particularly when carbon monoxide is required for the synthesis of alcohols and other compounds (see Fig. 16, page 126).

Vapor-phase reductions are, however, confronted with a number of technological problems: (1) limited per-pass conversion thus necessitating separation of aniline from nitrobenzene (unless the heat of reaction is gainfully employed this will constitute a significant item of expense); (2) formation of water as a coproduct which may adversely affect fixed catalysts and also introduce problems pertaining to the economic treatment of aniline-water solutions; and (3) sensitivity of catalytic operations which may result in overreduction and relatively low yields of amine compared with competitive processes.

No specific conclusions can be drawn regarding the groups of metals that are most effective. Although nickel and copper are considered the most active catalysts for a large number of hydrogenation processes, it is not always advisable in the reduction of nitro compounds to employ the most active catalysts. In fact, as will be shown later, it is known that different aromatic nitro compounds react with different intensity on the same catalyst. It has been found that the metals both preceding and following hydrogen in the electrochemical series can be used as catalysts. Thus, nickel, iron, tin, copper, silver, platinum, and gold are all mentioned in the patent literature.

The vapor-phase catalytic reduction of nitro compounds has been studied by O. W. Brown and his associates.[2]

Working under favorable conditions with a *nickel catalyst*, Brown and Henke obtained a 95 per cent yield of aniline from nitrobenzene. With a constant rate of flow of nitrobenzene, the yields drop off with too much or too little hydrogen. This fluctuation has been ascribed to over- or underreduction. Since nickel is such an active catalyst for this purpose, reduction of the aniline to cyclohexane and ammonia is known to take place.

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[1] *Reduction with Nickel.*—Brochet, Brit. 16,936, 22,523 (1913); U.S. 2,292,879 (1942).

With Tin.—Brown and Henke, U. S. 1,456,969.

With Copper.—Senderens, Fr. 312,615, and Schmidt, U. S. 1,237,828 (1917).

[2] *J. Phys. Chem.*, **26**, 161, 273, 715 (1922); **27**, 739 (1923).

When a catalyst prepared from precipitated *copper oxide* was used, the reaction was more moderate, and the yields under optimum conditions were uniformly good.

When *tin* was employed as a catalyst, excellent results were obtained in the reduction of nitrobenzene to aniline. The catalyst made from the hydroxide prepared by precipitation with sodium carbonate from a stannous chloride solution was the best.

The relative activity of some of the metal catalysts employed by Brown and Henke is shown in Figs. 3, 4, and 5. In Fig. 4, showing the effects of "rate of feed" for nitrobenzene, it can be seen that at only one point is the curve for tin below that of copper; in most places, the values for tin are above those for copper. Tin is likewise superior to nickel at all but the highest rates of feed; whereas at the lower rates, the yields with tin are far superior to those for nickel.

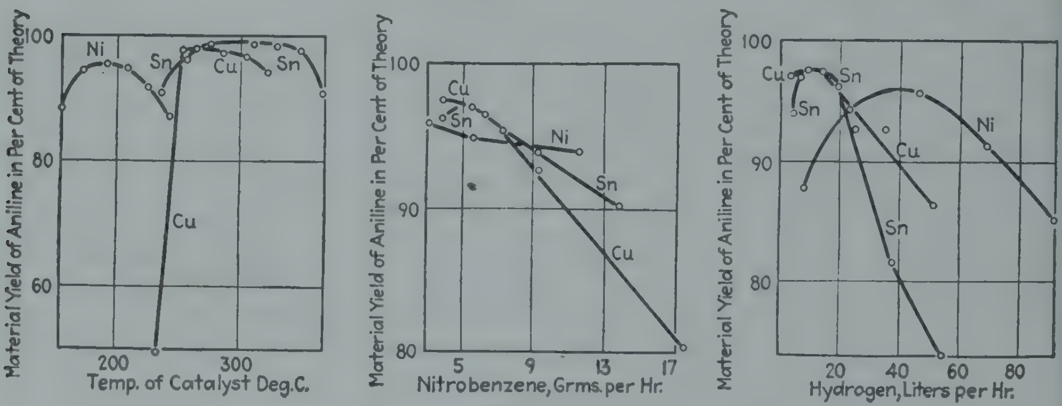


FIG. 3. FIG. 4. FIG. 5.

FIG. 3–5.—Vapor-phase reduction of nitrobenzene.

The effect of "flow of hydrogen" in the presence of the same catalysts is shown in Fig. 5. It will be noted that the curve for tin has a shape different from that of the other two curves. Thus, the decrease in yield with too much or too little hydrogen is more rapid for tin than with nickel or copper. However, the region within which high yields are secured is as wide or wider with tin than with other catalysts.

XII. DESIGN AND CONSTRUCTION OF EQUIPMENT

Materials of Construction.—Liquid-phase reductions are usually carried out in cast-iron vessels of various sizes. The larger ones (1,600-gal. capacity) are favored by plant engineers because of the possibilities of more economical operation. The standard machines made by a number of equipment manufacturers resemble one another quite closely. Each manufacturer has, however, introduced one or more accessories or refinements calculated to appeal to the experienced chemical engineer.

The iron reducers for iron-acid reductions are sometimes equipped with side and bottom cast-iron lining plates, which may be reversed or replaced, in order to protect the vessel against the continuous erosive action of the iron borings. Alternatively, the reducers may be lined to a limited extent with acid-resisting brick or tile. Such a protective coating lasts almost indefinitely and performs satisfactorily in service.

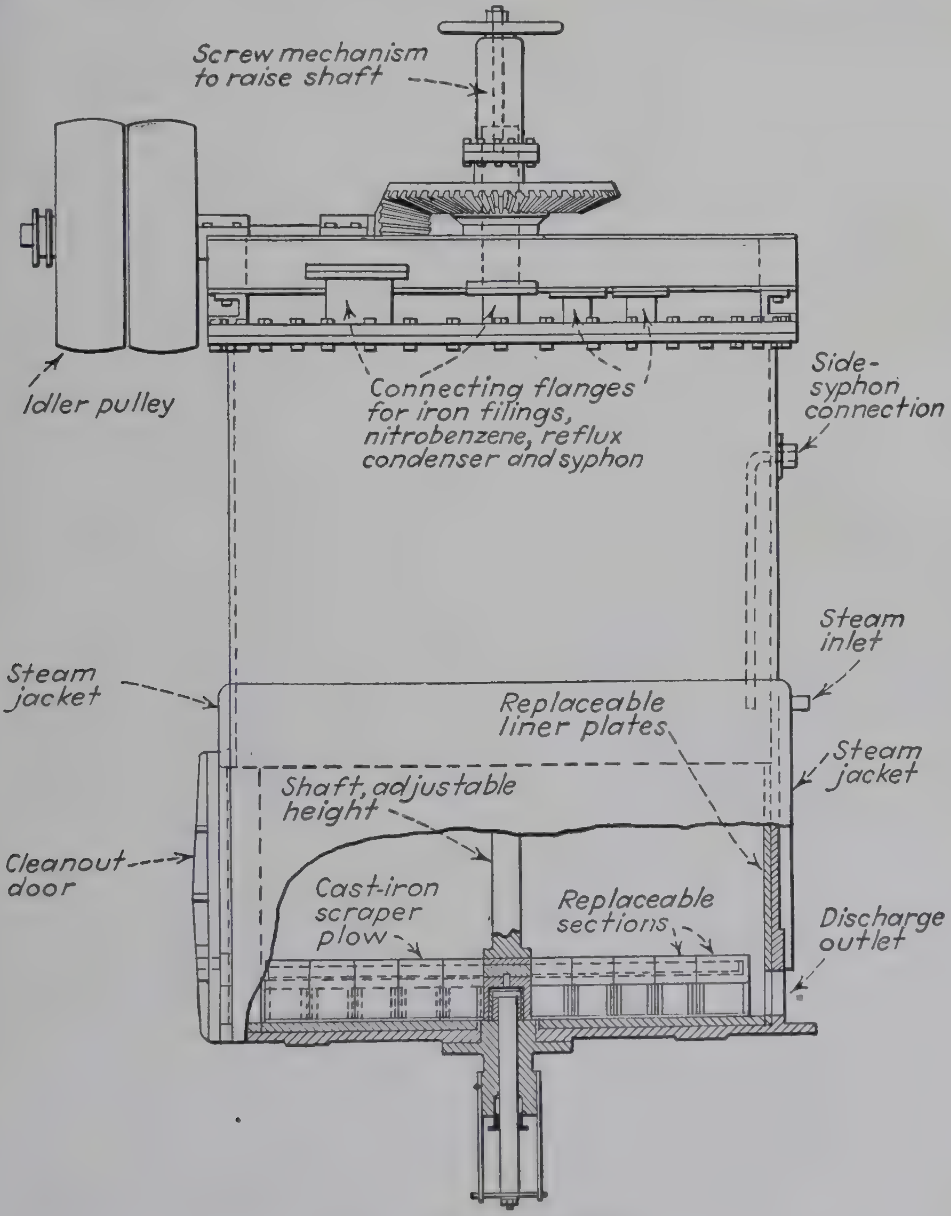

Screw mechanism to raise shaft
Idler pulley
Connecting flanges for iron filings, nitrobenzene, reflux condenser and syphon
Side-syphon connection
Steam inlet
Steam jacket
Replaceable liner plates
Steam jacket
Shaft, adjustable height
Cleanout door
Cast-iron scraper plow
Replaceable sections
Discharge outlet

Fig. 6.—Jacketed reducer.

The vessel is equipped with a nozzle at the base so that the iron oxide sludge or entire charge may be run out upon completion of the reaction. A wooden plug faced with iron disks and operated by a screw device fills the nozzle so that it is flush with the inside of the machine and makes an effective seal.

Wooden equipment is also used, particularly for the reduction of solid nitro compounds such as *p*-nitroaniline. These vessels are made of staves 2 to 3 in. in thickness, and the base is constructed of a double layer of 2-in. boards. Such tubs may range from 6 to 12 ft. in diameter and up to a height of 12 ft. They are equipped with wooden exhaust stacks to vent the vapors and gases liberated during the reaction. The top of such a reducer contains a large opening through which the solid nitro body, iron, and acid are delivered, and it is provided with a removable cover. Bronze pipes are employed for the introduction of steam to such reducers.

Agitation.—In some reducers, a vertical shaft carries a set of cast-iron plows which can be removed through the side door to the reactor (Fig. 6). These plows travel at the rate of 30 to 50 r.p.m. and serve to keep the iron particles in suspension in the lower part of the vessel. It will be recalled that the iron-acid reduction process is a three-component system, *e.g.*, reducible organic compound, acid, or metal salts and metal. Obviously, the best results in such a catalytic process can be obtained only when all three components are in intimate contact. If, in the reduction of nitrobenzene or similar compounds, the agitation is poor, most of the iron will be at the base, whereas the aqueous portion containing the acid or soluble metal salt will be at the top. It appears that an agitator of the type shown in Fig. 7 is more satisfactory, since it will be instrumental in bringing the iron particles to the upper portion of the reactor. It is recognized that such a sleeve-and-conveyor agitator needs to be made of material that will resist both the corrosion and erosion incidental to such reactions. A further advantage of this type of stirrer is the fact that the increased agitation assists in the diffusion of the amino compound away from the surface of the metal and thereby makes possible a more extensive contact between nitro body and catalytic surface. Fortunately, however, some of the deficiencies in mechanical agitation are balanced by the mixing provided by the molecular hydrogen that is generated in the reducer.

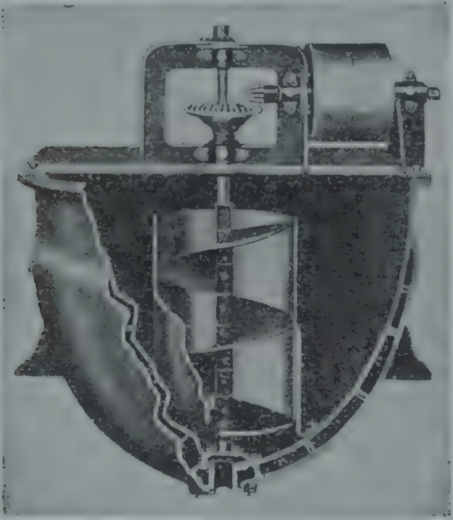


FIG. 7.—Sleeve-and-conveyor agitator.

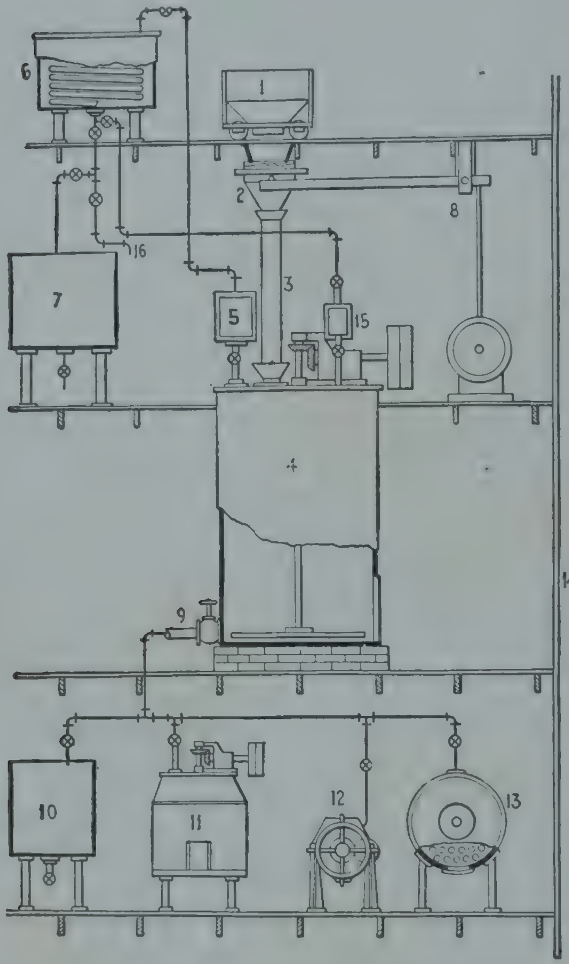
Advantages of Jacketed Reducers.—Practically all the iron reducers employed for the reduction of liquid nitro compounds are equipped with jackets. Although the reduction process is distinctly exothermic, the reaction proceeds best at slightly elevated temperatures, and it is customary therefore to warm the reactants at the start. Sometimes it is found necessary to add heat to maintain an active reaction, and it is generally necessary to do so to complete the reduction.

When jacketed reducers are employed, the heat is applied indirectly and no dilution of the charge occurs.. Under such circumstances, the optimum quantity of water can be delivered during the "feeding" stage, and the reaction is kept active by regulating the introduction of the reactants. When unjacketed vessels are used and live steam is introduced to maintain the reaction temperature, the charge becomes unduly diluted and reduces the concentration of the water-soluble catalyst and the rate of reaction. Furthermore, the liberated heat alone may not then be able to keep the system sufficiently hot. Such conditions lead to poor yields.

It is apparent that the introduction of excessive water also entails an increased cost in subsequent operations. It is immaterial whether the amine is a liquid or a solid or is recovered by fractional distillation or removal of water in a vacuum drier; any excess of water introduced during the reduction proper later requires a proportional amount of heat to effect its removal.

Reducer Accessories.—The reducer (Fig. 6) is, of course, equipped with a suitable feeding device, which will deliver the iron borings as required. The borings bin is frequently attached to a scale so that the charge entering the reducer is being weighed continuously and accurately (Fig. 8). Suitable flanged or screwed openings are provided for the introduction of the liquid nitro compound and catalyst solution. Steam connections are made in accordance with specific requirements, depending on whether or not the vessel is jacketed and whether or not the resulting amine is to be distilled with steam. A sight box, which is placed in the reflux line from the condenser to the reducer, is located over the reducer to enable the operator to watch the progress of the reduction. By means of a valve or gooseneck under the sight box, a heel of condensate is retained to prevent the escape of fumes from the reducer.

A very efficient and compact heat exchanger for condensing the vapors from the reducer consists of a closed tank completely filled with concentric layers of lead coils. Water at a high velocity circulates through the coils, entering at the top and discharging at the base. The vapors are distributed by a cylinder in the center of the condenser. The advantages of this heat exchanger are that it offers a maximum of surface to the vapors, no deposit or bubbles cover the outside of the coils to cut down the heat transfer, and the flow of cooling liquid is countercurrent to the ascending vapors. The condensed liquid collects in a lower cast-iron sleeve from which it flows back to either the reducer or the distilling tanks (aniline receivers) in the event that the reaction is completed and the amine is being distilled with steam.



1, delivery car for iron borings.
2, hopper and automatic feeder.
3, iron borings delivery line.
4, reducer.
5, baffle box.
6, condenser (note connections at base for refluxing or for distilling into.
7, crude receivers.
8, weighing apparatus for iron borings.
9, outlet valve to reducer leading to either
10, ordinary receiver used in syphon system.
11, vacuum distilling kettle.
12, filter press or
13, horizontal vacuum still.
14, elevator shaft.
15, sight box on reflux line.
16, safety drip which is kept open during reflux period to prevent contamination of system with nitrobenzene.

FIG. 8.—Plant assembly: reducer house.

XIII. TECHNICAL PREPARATION OF AMINES

The Manufacture of Aniline

An accurately weighed charge of nitrobenzene is delivered to the reducer from a lower floor level to avoid the danger of contamination, which is inherent in gravity-flow systems. About 10 to 20 per cent of the total iron, water, and catalyst is added, and the charge warmed to the reflux temperature, maintaining a constant effective agitation. The rate of reflux as observed in the sight glass must be quite vigorous, and the condensate fairly hot. If the reaction temperature is too low, intermediate compounds are formed, and these are later reduced to aniline only with great difficulty.

From an operating viewpoint, the process of feeding the reducer is a comparatively simple matter. A smooth reaction devoid of pressure peaks is obtained when the iron is uniform in quality and of a good physical character. It should preferably be delivered in small quantities to the boiling charge. The frequent delivery of small batches of iron minimizes the possibility of "sticking" the stirrers, due to the presence of an abnormal proportion of iron hydroxides. When a solid catalyst, such as ferrous chloride, sodium chloride, or sodium acid sulfate, is used, it is customary to feed it along with the iron, although theoretical considerations would suggest its complete introduction at the start. Such a practice, although simplifying the operation, may lead to excessive pressures. The water required for the hydrolytic reactions may be introduced in a number of ways. It may consist of (1) aniline waters recovered from certain steps in the operation; (2) dilute aniline-salt mother liquors when such a catalyst is available; (3) the aqueous solution containing the soluble active catalyst from a previous reduction; or (4), finally, it may be tap water that is used to wash down each addition of iron borings.

During the addition of iron, no external heat is required to carry on the reaction, as the reduction process is distinctly exothermic, about 1,900 B.t.u. being liberated per pound of nitro compound that is converted. It is necessary, therefore, to provide the most efficient type of condenser in order to maintain a rapid rate of reduction and to avoid excessive operating pressures.

Obviously, the preceding outline relating to the feeding of materials to the reducer is susceptible to many modifications. It is entirely feasible to add all the water, iron, and soluble catalyst at the start. This mass is then thoroughly heated and agitated to etch the iron. The aromatic nitro compounds can thereupon be introduced at definite time intervals, the precaution being taken that each portion is completely reduced before continuing with further addition. This technic gives satisfactory results in the reduction of many nitro compounds.

After all the reactants have been introduced, external heat is required to maintain a lively reflux. Steam may be introduced directly into the reducer charge, or it may be circulated through the jacket of the reducer. The condenser water is throttled down in order to avoid overcooling of the condensate, as this should be only slightly below the boiling point. As the reduction nears completion, the color of the distillate changes from orange to yellow and finally becomes colorless.

From an inspection of the equations representing the reduction process, the presence of combined aniline ($C_6H_5NH_3Cl$) in appreciable quantities would not be expected at the close of the reduction. The use of alkali to neutralize the charge, when small proportions of a chloride salt are used as catalyst, is then largely a precautionary measure, for it can be shown that the base has been set free almost in entirety by the hydrolytic action. The more highly dissociated ferrous chloride is, of course, concomitantly regenerated at the close of the reduction, and the test for soluble iron with sodium sulfide solution is very distinct. It is clear that the reaction represented below proceeds to the right most readily in the presence of metallic iron. In its absence, the weak base would be almost completely converted to the salt of the amine by the strong acid.

$$2R{\cdot}NH_3Cl + 2H_2O \overset{Fe}{\rightleftarrows} 2R{\cdot}NH_3OH + 2HCl$$
$$2HCl + Fe \rightarrow FeCl_2 + H_2$$

The introduction of alkali does, however, break up soluble iron aromatic compounds, such as hydroxylamine derivatives. Furthermore, it makes possible a more rapid distillation of the amine, as the introduction of the common ion $O\bar{H}$ reduces the solubility of aniline in water. In the preparation of water-soluble amines, neutralization of the charge is desirable only when the crude product is to be dehydrated and purified by distillation. The preparation of *p*-phenylenediamine is such an example. When the soluble amine is recovered by partial dehydration and crystallization, the faintly acid mother liquors, containing the active catalyst, can be used in subsequent reductions.

IMPORTANCE OF CHEMICAL ENGINEERING IN LOWERING COSTS

The most important problem in the preparation of aniline relates to its separation from the reducer charge. The problem is essentially one of chemical engineering. The engineer's goal is to provide for the continuous mechanical separation of the aniline and water from the iron oxide sludge and to recover the latter as a finely divided dry powder of commercial value. The aniline oil should then be separated from the water in a reasonably pure state, the amine going to the storage for final distillation (Fig. 9), while the aqueous solution containing dissolved catalyst and some amine is returned to the reducer. Groggins, in a survey of the processes for the manufacture of aniline, shows that a great economic advantage accompanies the choice of an efficient separating scheme.[1] In this work, the following criteria are suggested as a guide in the selection of equipment: (1) *Simplicity*. Minimum handling of material. (2) *Yields*. Reduction to a minimum of the known sources of loss. (3) *Productivity*. Discharging the batch immediately after reduction is complete. (4) *Water Balance*. Elimination of methods that cause an accumulation of aniline water, as this involves a great loss in yield and an increase in power costs. (5) *Power Load*. The consumption of steam, water, and electricity is an important factor in determining the cost. (6) *By-product Sludge.* In some localities, a market can be obtained for a dry, clean, finely divided, aniline-free iron oxide. These criteria will be better appreciated by reviewing some of the methods for separating the aniline from the reducer charge. These will be presented very briefly, giving due attention to the underlying economic factors.

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[1] GROGGINS, "Aniline and Its Derivatives," D. Van Nostrand Company, 1924.

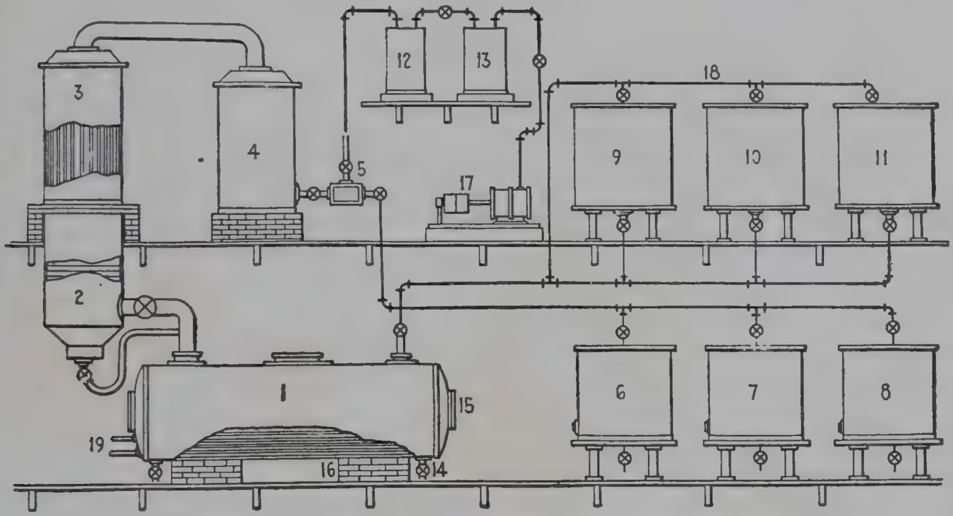
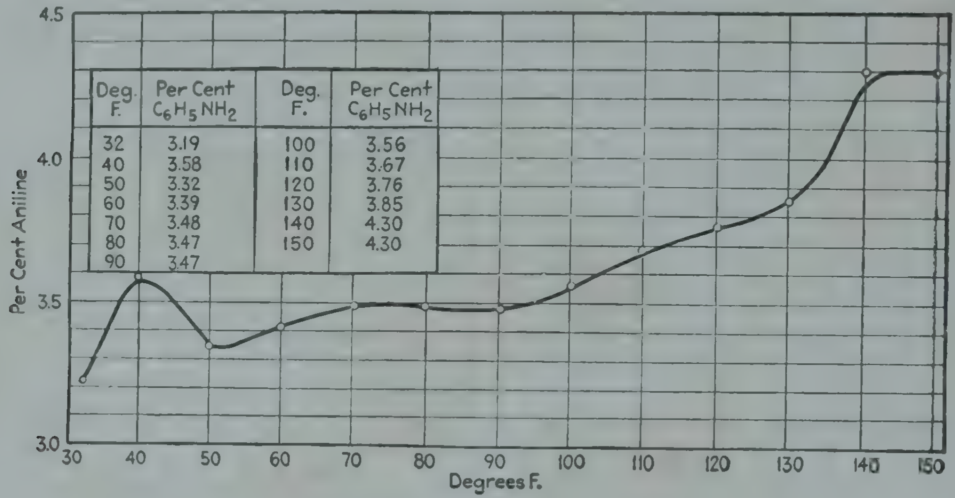


Fig. 9.—Aniline distillation: plant assembly.

1, horizontal still, completely lagged; 2, dephlegmator; 3, dephlegmator condenser; 4, condenser; 5, sight box with connection leading to 6, 7, 8, receivers for pure aniline; 9, 10, 11, crude-aniline reservoirs; 12, 13, catch-all tanks for aniline vapors; 14, bottom outlet to still; 15, clean-out hole; 16, horizontal steam coils in still; 17, vacuum pump; 18, vacuum feed line from crude-aniline reservoirs to still; 19, outside steam connections to still.

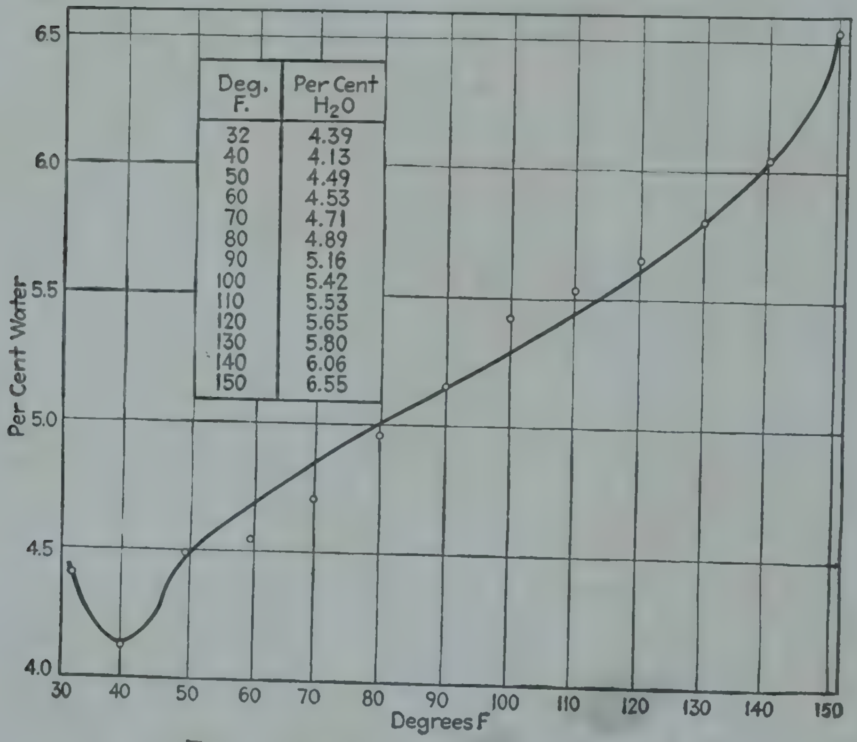
Method I. Steam Distillation of Aniline from the Charge and Treatment of Aniline Water in Stills.—This is one of the first and most costly systems. After reduction is complete, the reflux from the reducer condensers is directed to a receiving tank, and live steam is introduced to carry on the distillation. It is obvious that a large quantity of water is thus introduced into the system. The distillate in the receiving tank is permitted to cool, and the heavier oil is drawn off and delivered to the rectifier. The aniline water, containing from 3.5 to 5.0 per cent amine (Figs. 10, 11), is drawn from an upper valve and pumped to storage tanks. It is usually made slightly alkaline prior to its being delivered to the aniline-water stills. The latter are usually long horizontal tanks provided with steam coils. When half of the charge is distilled, the residual liquor shows only a trace of aniline. The distillate is cooled and settled, and the aniline that separates out owing to its increased concentration is removed. The aniline water is again returned to the system and treated again. It is evident that in this steam-distillation process, the material must be handled considerably. The method is, furthermore, objectionable, as it curtails production because the reducer is used as a still.

Steam Distillation from Jacketed Reducers.—When the reduction takes place in a jacketed reducer, a slight improvement is realized. This is due to the fact that the jacket cuts down the dilution during the reduction period. Furthermore, some of the ensuing distillate is fortunately consumed in the reduction of the next charge. Finally, less steam is required during the distillation period, owing to the increased aniline concentration in the reducer charge.



Deg. F.	Per Cent $C_6H_5NH_2$	Deg. F.	Per Cent $C_6H_5NH_2$
32	3.19	100	3.56
40	3.58	110	3.67
50	3.32	120	3.76
60	3.39	130	3.85
70	3.48	140	4.30
80	3.47	150	4.30
90	3.47		

FIG. 10.—Solubility of aniline in water.



Deg. F.	Per Cent H_2O
32	4.39
40	4.13
50	4.49
60	4.53
70	4.71
80	4.89
90	5.16
100	5.42
110	5.53
120	5.65
130	5.80
140	6.06
150	6.55

FIG. 11.—Solubility of water in aniline.

Steam Distillation and Nitrobenzene Extraction of Aniline Waters.—The procedure in this system is identical with the preceding up to the point where the aniline oil is drawn off from the settling tanks. The supernatant water is now treated with nitrobenzene intended for the reducer house. Two extractions are made on each batch of aniline according to the flow sheet shown in Fig. 12, after which the water is practically free of both aniline and nitrobenzene.

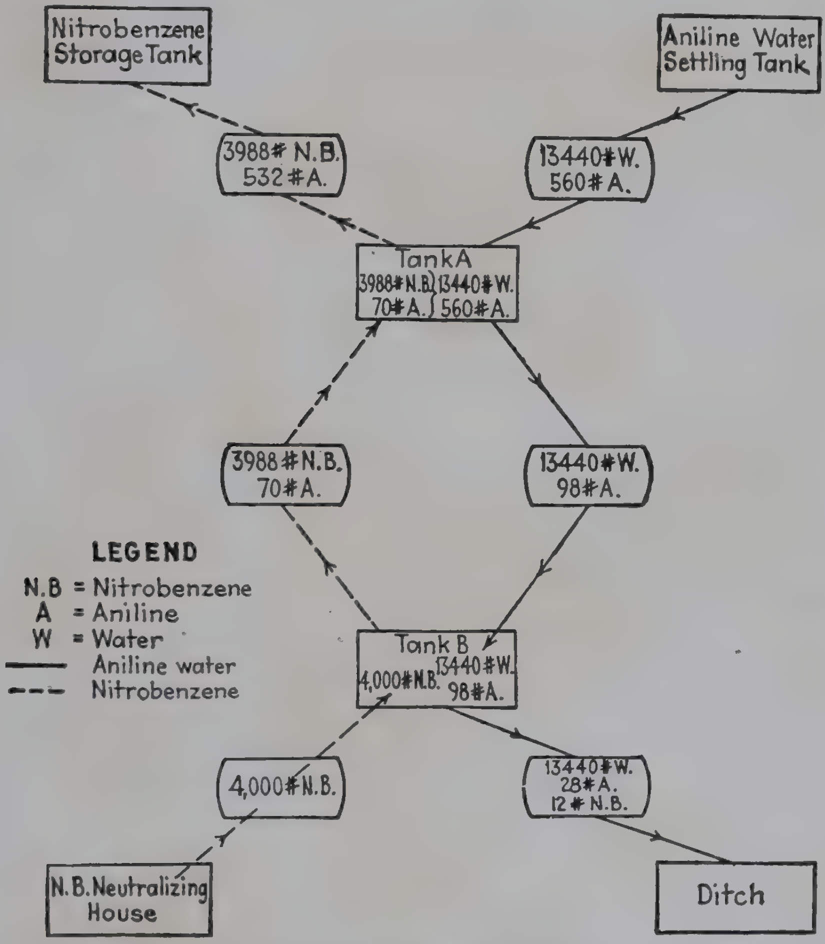

Nitrobenzene Storage Tank
Aniline Water Settling Tank
3988# N.B. 532#A.
13440#W. 560#A.
Tank A
3988#N.B. 70#A.
13440#W. 560#A.
3988#N.B. 70#A.
13440#W. 98#A.
LEGEND
N.B = Nitrobenzene
A = Aniline
W = Water
Aniline water
Nitrobenzene
Tank B
4,000#N.B.
13440#W. 98#A.
4,000#N.B.
13440#W. 28#A. 12#N.B.
N.B. Neutralizing House
Ditch

FIG. 12.—Flow sheet: nitrobenzene extraction of aniline.

Steam Distillation in Conjunction with Aniline Boiler.—The practice of using the surplus aniline water in a boiler to generate steam for use in the reducers is one that formerly found considerable favor in Europe. The operation calls for a large aniline-water reservoir to which all the water from the settling tanks is delivered. From a side valve considerably above the base of the tank, the water is drawn off and delivered under pressure to the boiler. The steam line from the boiler is led to the reducers and is connected separately, so that "pure" steam can be used to complete the reduction and distillation. It is apparent that this is a fairly economical method of treating distillation waters. Precautions must be taken to neutralize the aniline waters in order to diminish boiler-tube troubles, which are one of the disturbing features of this system.

Method II. Jacket Reduction and Vacuum Still.—This system involves the use of a large cast-iron vacuum still into which the reducer charge runs by gravity. As soon as delivery is complete, the reducer is prepared for the next run, and the distillation of the finished charge started. Inasmuch as the distillation is carried on *in vacuo*, the aniline water comes over first, and then a mixture containing increasing proportions of aniline, until all the water is removed. The aniline content is about half distilled by the time water-free aniline is obtained. This fraction continues only for a short time, when the distillate is darkened by contamination with the residual sludge. The installation of an auxiliary dephlegmator makes possible a better separation, but this, of course, entails an additional cost.

The system works fairly satisfactorily, the greatest difficulty being the reduction of the aniline content of the iron oxide sludge. When the residual amino content is about 10 per cent, the charge becomes gummy, and a tremendous load is put on the stirring mechanism. This condition prevails until the oxide granulates and falls over the plows. Approximately half the operating time is consumed in recovering the last 10 per cent of the yield. When the distillate is reduced to negligible proportions, the dry sludge is discharged into industrial cars.

An analysis of the hot residue, which is very fine and dusty, shows that it is practically all magnetic iron oxide. As it is hot, the surface material sets up an oxidation with the formation of the red Fe_2O_3. Analytical tests show that considerable aniline remains behind unless long drying periods are provided.

A modification of the preceding method is carried out as follows: The reducer charge is dropped into a large horizontal vacuum tank that is fitted with a large number of welded, seamless, extra-heavy steam pipes. Heat is applied as before, and the distillation proceeds even more rapidly on account of the greater heating surface. At the close of the distillation, the manhead to the vacuum tank is removed, and the dry iron oxide flushed out at the base by means of a powerful stream of water.

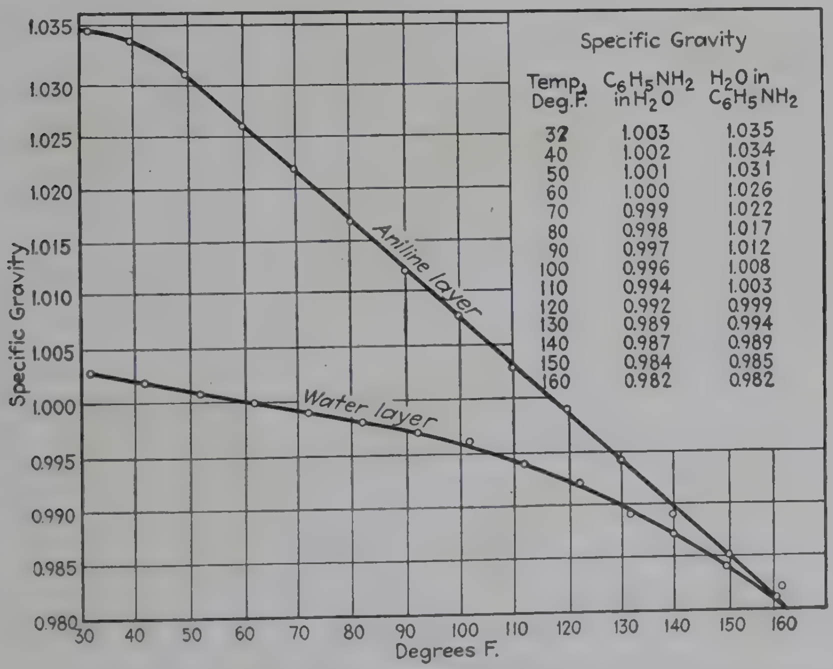
The vacuum-distillation system may be further modified by distilling with live steam the final 10 per cent of aniline. Such a practice does not introduce a large quantity of water into the system and saves considerable time. The vacuum-distillation system apparently doubles the productivity of the reducers; but since the cost of the stills is quite as great, the saving is more apparent than real.

Method III. Filtration of Reducer Charge.—In this system, the entire charge from the reducer is delivered to a large filter box. Since the sludge retains considerable aniline, the cake is first washed with a stock solution of aniline water and then with fresh boiling water and then blown with hot air or steam. This procedure leaves about 8 per cent aniline water of 5 per cent aniline content with the sludge and constitutes a loss of less than 1 per cent of the total yield. Some of the advantages of filtration separation are:

1. Simplicity of operation.
2. Low operating cost.
3. Increase in productive capacity of reducers.
4. Elimination of cooling water and lowering of steam and power costs.
5. Compact system, making for good yields.

The success of this procedure depends on the solution of the unit operation —filtration. The reducer charge contains iron hydroxides and filters very poorly. It is necessary, therefore, to effect the filtration in stages through metal screens, preferably after the introduction of an electrolyte to expedite the precipitation of colloidal iron compounds. The filtrate can be settled for the separation and decantation of aniline. The sludge can be washed on the screens with some aniline water, and then the final traces of amine are removed by distillation or washing with steam.

Method IV. Syphon Separation.—The introduction of a syphon into the reducer at the completion of the reduction stage to draw off the supernatant oil from the lower aqueous layer is a convenient and inexpensive method of effecting the separation. A glance at the specific gravity curves (Fig. 13) reveals that the aniline oil layer becomes lighter than water above 71°C. (160°F.). The separation is accelerated and made sharper by the addition of salt, which increases the density of the aqueous layer and decreases the solubility of aniline therein.



Specific Gravity

Temp. Deg. F.	$C_6H_5NH_2$ in H_2O	H_2O in $C_6H_5NH_2$
32	1.003	1.035
40	1.002	1.034
50	1.001	1.031
60	1.000	1.026
70	0.999	1.022
80	0.998	1.017
90	0.997	1.012
100	0.996	1.008
110	0.994	1.003
120	0.992	0.999
130	0.989	0.994
140	0.987	0.989
150	0.984	0.985
160	0.982	0.982

FIG. 13.—Temperature-specific gravity curves: aniline water system.

Jacketed reducers are used in this system, and reduction is effected by the use of external heat. Owing to the fact that there is a slight loss of water during the reduction process, it is necessary to provide sufficient at the start to ensure fluidity. An excessive water content, however, distinctly slows up the reduction on account of the lower concentration of soluble catalyst.

The syphon is usually an inverted funnel operated by a worm drive and enters the vessel through a tight stuffing box. During the operation, it is worked up toward the top of the reducer so as to clear the paddles or other type of stirring mechanism. An alternate scheme utilizes a bent tube for withdrawing the aniline. A 2-in. pipe penetrates the side of the reducer through a stuffing box above the jacket line, and an improvised gauge on the outside of the reducer indicates the position of the bend on the inside. By this means, it is possible to lower the syphon end accurately to the desired level and later raise it out of the sphere of agitation. This scheme avoids almost completely any stoppage and breaks in the draw-off line, difficulties that are encountered when the syphon is suspended from the top cover of the reducer.

After reduction is completed, 5 to 10 per cent by weight of salt (compared with nitrobenzene used) is added, and the agitation continued until the sodium chloride is completely dissolved. Agitation is then stopped; the plows are raised above the sludge; and the charge allowed to settle. Steam is kept on the jacket to maintain a temperature of 85 to 90°C. in the reducer. The introduction of a demulsifying agent along with the salt has been suggested for expediting the separation of the layers.

After settling about 1 hr., a slight vacuum is put on the receiving tank and the syphon mechanism lowered to the desired level. A sight glass on the delivery line indicates the rate of delivery and the quality of the aniline. If too great a vacuum is used, considerable turbidity results. The tube is lowered slowly until the sight glass indicates that the aniline is being contaminated with considerable water.

The remainder of the charge consists of aniline water and iron oxides. With continued stirring, live steam is admitted until the batch is free of aniline. The final distillation may be made in a separate still when production requirements justify such an installation. In view of the fact that only a small quantity of aniline remains after the separation, very little time and steam are consumed in the final operation. In fact, the aqueous layer may be returned to the reducer for the next charge and thus save the bulk of the soluble catalyst. Still another use for the aqueous layer is its utilization in washing the nitrobenzene intended for the reducer house. These alternative methods save the expense of steam distillation and, incidentally, serve a useful purpose in the scheme of operations.

The syphon system is indeed attractive, as it is easily adapted to xisting plants. It is compact, economical, and devoid of aniline-water roblems. The cost of salt, the use of which may be dispensed with, is uite insignificant when compared with the cost of steam necessary to istill the aniline from the reducer charge. A filter box can be used to dvantage in order to eliminate the fine iron oxide that is drawn over with he aniline. These boxes are constructed so that they can be opened and leaned in a few minutes; and if necessary, a new filter plate may be nstalled. In all cases, it is advisable to clarify the aniline by some method before submitting it to final distillation.

In the syphon system of aniline oil separation, the cost of installation and maintenance is very low, less machinery being used than in any of the other systems. There is also a minimum of handling of the amine, which is reflected in better operating yields.

Owing to the fact that the sludge has to settle out to effect a satisfactory separation, a mechanical problem is presented in providing a proper type of transmission to permit resumption of agitation after the aromatic compound is drawn off. When fine iron borings are used and are fed in small portions, the resultant sludge should not cause any transmission trouble. In fact, in some reductions (*p*-nitroaniline to *p*-phenylenediamine), it is quite customary to permit the reduced charges to stand overnight. When, however, the transmission apparatus is designed to permit the raising of the stirrer (see Fig. 6), no difficulty is experienced in restarting.

TABLE VI.—MANUFACTURE OF ANILINE. ECONOMIC SURVEY

Type of Separation	Cost per 1,000 Lb. of Aniline
Steam distillation of aniline in nonjacketed reducer	$12.81
Steam distillation of aniline in jacketed reducer	10.26
Steam distillation of aniline: nitrobenzene extraction of aniline water: Nonjacketed reducers	8.16
Steam distillation of aniline: nitrobenzene extraction of aniline water: Jacketed reducer	6.15
Use of aniline boiler to generate steam from aniline water	4.11
Jacket reduction, accompanied by vacuum still	3.11
Filtration of reducer charges	1.20
Syphon separation, according to modifications	1.00–4.25

Economic Summary.—It would be misleading to draw conclusions solely from the data just presented regarding the known sources of loss in the various methods of separating the aniline from the charge. A number of other factors enter into the preparation of the cost sheet besides the tabulation of comparative losses and power charges. The figures do present, however, the known possible efficiencies that may be expected from the several modifications of this unit process. If the variables of operating efficiencies are disregarded for a moment, the apparent comparative charges for separating the crude aniline from the reducer charge are as shown above in Table VI.

Cost Factors in Production of Aniline

Reduction of nitrobenzene to aniline:	
Molecular weight benzene (C_6H_6)	78
Molecular weight nitrobenzene ($C_6H_5NO_2$)	123
Molecular weight aniline ($C_6H_5NH_2$)	93
Theoretical yield of aniline per 100 lb. benzene	119.2
Standard yield of aniline per 100 lb. benzene	109.75
Theoretical yield of aniline per 100 lb. nitrobenzene	75.6
Standard yield of aniline per 100 lb. nitrobenzene (98%)	74.0
Materials to produce 100 lb. aniline from nitrobenzene:	
126 lb. nitrobenzene, at $0.05	$6.30
140 lb. iron borings, at $0.0075	1.05
15 lb. HCl (or equivalent) at $0.01	0.15
Total material costs	$7.50
Operating costs: Labor operating Repairs Supplies Direct supervision	$1.00
Power costs: Electricity Steam Air Water	0.30
Overhead: Administration Depreciation Insurance Fixed charges	0.35
Plant cost per 100 lb. aniline	$9.15

Aniline Cost Data Analysis[1]

$$\text{Operating costs} = \frac{1.00}{9.15} = 10.93\% \text{ total cost}$$

$$\text{Power costs} = \frac{0.30}{9.15} = 3.28\% \text{ total cost}$$

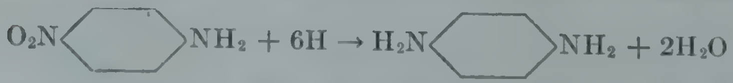
$$\text{Overhead} = \frac{0.35}{9.15} = 3.82\% \text{ total cost}$$

$$\text{Raw materials} = \frac{7.50}{9.15} = 81.97\% \text{ total cost}$$

[1] Numerator = cost of each phase of production.
Denominator = total net cost.

The Manufacture of Paraphenylenediamine

Reduction of Paranitroaniline with Iron and an Acid



p-Phenylenediamine is manufactured commercially by the reduction of *p*-nitroaniline. This reduction is quite similar to that of aniline, and its technic is subject to some of its numerous modifications.

The process may be conveniently divided into four steps, which are s follows:

1. Reduction of the *p*-nitroaniline to *p*-phenylenediamine.
2. Filtration of the reduction batch.
3. Dehydration of filtered liquor.
4. Vacuum distillation of crude *p*-phenylenediamine.

The Reduction.—A large wood vat is used to carry on this operation (Fig. 14). The batch is stirred by means of a steel shaft which carries two or more sets of plows. A heavy-duty motor is provided to take care of the heavy initial reduction load and also when starting up tubs that have been left quiescent overnight. Two tubs are required for plant operations. One is used for preparing a new batch while the other is delivering the reduced charge to the filter.

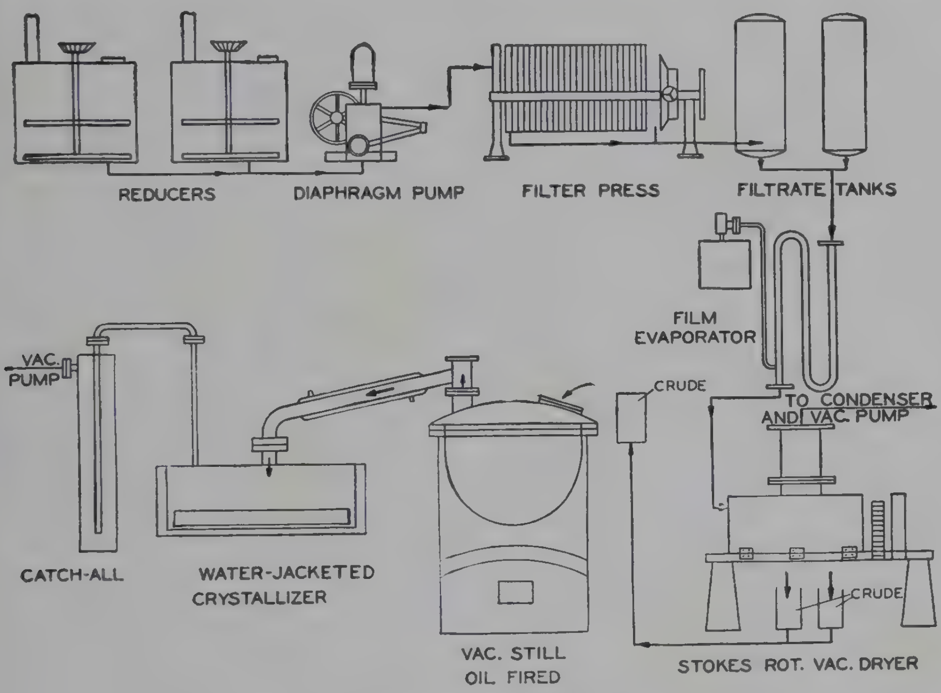

REDUCERS
DIAPHRAGM PUMP
FILTER PRESS
FILTRATE TANKS
FILM EVAPORATOR
VAC. PUMP
CRUDE
TO CONDENSER AND VAC. PUMP
CATCH-ALL
WATER-JACKETED CRYSTALLIZER
VAC. STILL OIL FIRED
CRUDE
STOKES ROT. VAC. DRYER

FIG. 14.—*p*-Phenylenediamine plant.

The operation is started by pumping up sufficient wash water from previous charges to cover the paddles of the agitator. The stirrers operating at 40 r.p.m. are then started, and 1,000 lb. of iron borings is slowly put into the tub. One hundred pounds of 20°Bé. hydrochloric acid is then added, and the mixture agitated and heated until the iron is etched and a good paste of ferrous chloride is made. It should react immediately and distinctly when spotted with a weak sodium sulfide solution. Either dry or moist *p*-nitroaniline is then introduced, about 50 lb. at a time. After each addition, sufficient time must elapse to ensure the presence of ferrous chloride, for it will be noticed that the spot test for soluble iron fails immediately after the addition of nitro compound. The charge must be kept sufficiently warm so that a foaming reaction prevails. It has been found that a ratio of 1.20 lb. of iron to 1 lb. of *p*-nitroaniline (molar ratio 3:1) gives the best results, although it is possible, as in the production of aniline, slightly to lower this ratio. Toward the close of the feeding operation, the balance of iron necessary for reduction is introduced. Thus, when 750 lb. out of a total of 1,200 lb. of nitro compound has been fed into the vat, the balance of approximately 500 lb. of fine iron is added.

Toward the end of the run, the reaction slows down, and it is necessary to introduce steam to carry on and complete the reduction. The test for soluble iron also becomes less distinct. As long as there is any *p*-nitroaniline present, a yellow spot test will be obtained on filter paper. *p*-Phenylenediamine yields a purple spot with a perfectly clear ring around the sludge spot. It is always advisable to test for soluble iron with sodium sulfide to ensure completeness of reduction. If the reduction is not carried on at the boiling temperature, intermediate azo and hydrazo products are sure to be formed. These are not so easily reduced and cause a lowering of the yield.

In order to prevent any oxidation of the *p*-phenylenediamine liquor prior to filtration, it is advisable not to neutralize the charge until this phase of the process begins. An excess of soda ash is used, and a test for alkalinity with phenolphthalein is required. Two pounds of sodium bisulfite and 3 lb. of sodium sulfide (30 per cent crystals) are then added to precipitate soluble iron salts and to ensure against subsequent oxidation. About 12 hr. are required to feed the nitro compound into the reducer.

Filtration of Reduction Batch.—A large plate-and-frame filter is customarily used to separate the residual iron sludge from the *p*-phenylenediamine liquor. The press is fitted up with a pump for delivering the charge from the tubs. Air and water lines and an ejector for delivering hot water during the washing period complete its accessories. The press is first warmed by passing in live steam, and the delivery pump started. The filtrate is tested for completeness of reduction and for clarity. A spot on filter paper should be very light purple with no traces of yellow. The presence of a blue tint indicates the formation of indulines.

As soon as the batch is on the filter, it is washed with wash water from previous batches. This liquid follows the rest of the batch into one of two storage tanks that are placed below the press level, so that the filtrate flows into them by gravity. Hot water is then introduced into the press, and this filtrate runs into a large tank. Sufficient hot water is used to maintain a water balance, *i.e.*, to have sufficient to provide a heel for the reducer tub and to replace the original mother liquor on the filter. The filter is then blown with air until the cake is dry.

The cake is dropped into a pan underneath the press and removed. It is analyzed regularly for amino content.

Dehydration of Diamine Liquor.—The filtrate from the press is a dilute solution of *p*-phenylenediamine containing a small amount of iron oxide in suspension. Since only 936 lb. of *p*-phenylenediamine can be theoretically obtained from 1,200 lb. of *p*-nitroaniline and about 9,000 to 10,000 lb. of water is used during the reduction, it is manifest that a 10 per cent solution of phenylenediamine is delivered to the liquor-storage tank. Although it is feasible and practicable to deliver a solution of such strength directly to the drier, it is more economical from the standpoint of both yield and steam consumption first to concentrate this liquor. Two-stage vertical evaporators and film evaporators have been used successfully for this purpose. A steam-jacketed vacuum drier of suitable dimensions can be used for effecting the final dehydration. On top of the drier is an upright steel shell 2 ft. in diameter and 4 ft. high, packed with suitable material to prevent entrainment, that leads to a tubular condenser. A sight box at the base of the condenser permits the operator to inspect the condensate. This should not contain more than a trace of color; otherwise, a loss of *p*-phenylenediamine is indicated. When the sight box indicates that most of the water has been distilled off, the jacket steam pressure is reduced from 15 to 5 lb. and after 1 hr. turned off completely. If the batch in the drier is now further agitated for 1 hr., it will be ready for dumping. A sample must always be first taken to ensure absolute dryness. The crude product must be black with a purplish tinge. A gray tinge indicates moisture. The presence of 1 per cent water in the crude product is detrimental to the production of a good *p*-phenylenediamine.

The material in the drier is discharged into large steel cans and weighed. From this weight, the yield of crude *p*-phenylenediamine is obtained, and the charges for the vacuum still are made up. It is advisable to analyze the crude *p*-phenylenediamine for salt and iron at regular intervals, as these figures give valuable information regarding the operations. About 82 lb. of crude products is obtained for every 100 lb. of *p*-nitroaniline reduced.

Vacuum Distillation of Crude *p*-Phenylenediamine.—A cast-iron still (Fig. 15) capable of holding 1,000 lb. of crude *p*-phenylenediamine is placed on a masonry setting, and a solid arch built underneath it so that it runs back within 10 in. of the rear wall. In this way, the heat furnished either by gas or by fuel oil reaches the still mainly by radiation. When optimum conditions prevail, the temperature of the batch in the still will be 230 to 250°C., and the temperature of the vapors in the line leaving the still will be 180 to 190°C. It is essential that an efficient vacuum pump be installed on this system in order to obtain a very attractive crystalline product. The crystallizing pans that receive the condensed vapors from the still are placed into water-cooled castings. At the close of each run, the pans are allowed to stand and cool for several hours and then pulled out. It is necessary to cool the distilled product about 36 hr. before breaking it up, as it remains molten on the inside for a long time. It is also true that its color deteriorates if the fused cake is broken prematurely.

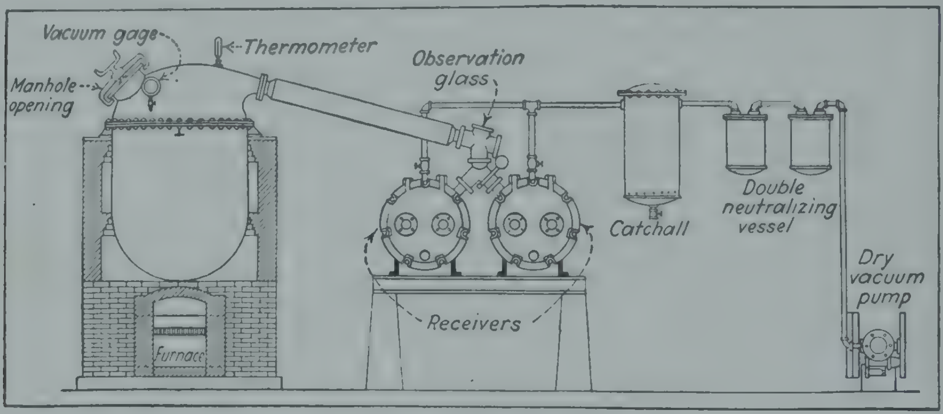


FIG. 15.—Vacuum distillation plant for *p*-phenylenediamine.

If the crude is moist, the final product will be very poor and sometimes be sloppy. A distinct red coloration of the finished product indicates either moisture or acidity in the crude product.

Yields.—The yields obtained by the process outlined above should be about 90 per cent of theory, or slightly over 70 lb. of finished *p*-phenylenediamine per 100 lb. of *p*-nitroaniline used. The sources of loss in the system are

Reduction	3 %
Filtration	1½ %
Dehydration	1½ %
Distillation	3 %
Total	9 %

COST OF MATERIALS USED IN REDUCTION

Reduction	*p*-Nitroaniline	1,200 lb.	at $0.40	=	$480.00
	Iron borings	1,460 lb.	at 0.013	=	18.98
	Hydrochloric acid	115 lb.	at 0.01	=	1.15
Neutralization	Sodium carbonate	60 lb.	at 0.012	=	0.72
	Sodium sulfide	4 lb.	at 0.02	=	0.08
	Sodium bisulfite	2 lb.	at 0.05	=	0.10
Cost of raw materials					$501.03
Cost of raw materials per 100 lb. *p*-phenylenediamine based on yield of 70.1 lb. per 100 lb. *p*-nitroaniline used					$59.56

Based on a monthly production of approximately 20,000 lb. of *p*-phenylenediamine, he factory cost data per 100 lb. of product will be close to the following:

Raw materials	\$59.56
Operating charges	4.30
Power charges	4.20
Plant overhead	3.54
Plant cost per 100 lb. *p*-phenylenediamine, exclusive of package, storing, and sales expense	\$71.60

An analysis of the cost elements again reveals the importance of obtaining high operating efficiencies:

Percentage cost of raw materials	$\frac{\$59.56}{\$71.60}$	= 83.2%
Percentage cost of operation	$\frac{\$4.30}{\$71.60}$	= 6.0%
Percentage cost of power	$\frac{\$4.20}{\$71.60}$	= 5.9%
Percentage cost of plant overhead	$\frac{\$3.54}{\$71.60}$	= 4.9%

Alkali-sulfide Reductions

m-NITROANILINE FROM *m*-DINITROBENZENE

One hundred parts of *m*-dinitrobenzene is added to 1,000 parts of water at 90°C. contained in a reducer fitted with a reflux condenser and a propeller-type stirrer. Upon emulsification, 245 parts of sodium sulfide ($9H_2O$), dissolved in a minimum of water, is gradually run in. The dinitro compound is gradually reduced to *m*-nitroaniline, the end point being determined by the formation of a definite black streak when ferrous sulfate solution is added to filter paper spotted with some of the reducer liquor.

The preceding process has been modified by Lyford, who uses an organic solvent, which is immiscible with water, for the *m*-dinitrobenzene.[1] Accordingly, 100 parts of technical dinitrobenzene, 90 per cent purity, and 160 parts of either solvent naphtha or toluene are put into the reducer, and the mixture is warmed to 60°C. to effect solution. Then, 4,000 parts of hot water is added, and the *m*-dinitrobenzene solution is stirred and heated to 95°C. A hot polysulfide (Na_2S_3) solution—made by heating 720 parts of 7 per cent Na_2S with 40 parts of flowers of sulfur—is then added rather rapidly. The reaction of the polysulfide is distinctly exothermic, and the charge boils vigorously, but overheating is avoided because of the vaporization of the solvent. Reduction of the dinitrobenzene to *m*-nitroaniline is found to take place very quickly under such conditions.

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[1] Lyford, U. S. 1,878,950 (1932).

The hot reduction mass is first filtered to remove any free sulfur, and the solvent naphtha in the filtrate is distilled with steam. The dissolved *m*-nitroaniline crystallizes out in the form of bright yellow crystals when the residual liquor is cooled. After washing, the product has a melting point of about 113°C. (c.p. = 114°C.) and can be used directly in the manufacture of azo dyes. A yield of approximately 90 to 92 per cent of theory is attainable, and the process is applicable to other *m*-dinitro compounds, *e.g.*, the *m*-dinitro derivatives of toluene and xylene.

Preparation of 5-Nitro-1-Naphthylamine

When naphthalene is dinitrated, a mixture of 1, 5- and 1, 8-dinitronaphthalenes is obtained. Upon reduction under controlled conditions with sodium sulfide, the 1, 5-isomer is partially reduced selectively, but the 1, 8-derivative remains substantially unaltered.[1] Thus, a suspension of 55 parts of the mixture of isomerides in 400 parts of water is heated to 90°C., and a solution containing 23.2 parts sodium sulfide crystals and 6.2 parts of sulfur in 80 parts of water is added. The mixture is stirred for 15 min. and then cooled and filtered. The residue on the filter is washed with water and then is treated with dilute hydrochloric acid to dissolve any nitroamino compound. The acid mixture is filtered, and the residue, which is relatively pure 1, 8-dinitronaphthalene, is washed with water. The filtrate contains the hydrochloride of 5-nitro-1-naphthylamine.

Preparation of 2, 4-Aminonitrophenol from 2, 4-Dinitrophenol

This reduction is made by adding 90 parts of an aqueous solution containing 17 parts of sodium sulfide to a solution of 60 parts ferrous sulfate dissolved in 80 parts of water.[2] The mixture is thoroughly stirred until a suspension of freshly precipitated ferrous sulfide is obtained. There is then added 20.6 parts of the sodium salt of 2, 4-dinitrophenol dissolved in 160 parts of water, and the mixture is heated gradually to approximately 60 to 80°C. until the reduction of one nitro group is complete.

The charge is then filtered, and the filtrate exactly neutralized by the addition of hydrochloric acid. The precipitated 4-nitro-2-aminophenol is then filtered off.

Preparation of -2-Amino-7-Chloroanthraquinone

The procedure recommended by Gubelmann shows that 2-nitro-7-chloroanthraquinone can be reduced satisfactorily in alkaline sulfide solutions without appreciable replacement of the chloro substituent.[3]

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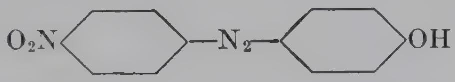
[1] Hodgson, U. S. 1,988,493 (1935).

[2] Dieterle, U. S. 1,689,014 (1928).

[3] Gubelmann, U. S. 1,810,012 (1931).

This procedure is of interest in view of the fact that the halogen substituent is loosely bound by virtue of the presence of the $-NO_2$ and $>CO$ groups. The reduction is carried out by suspending 287 parts of 2-nitro-7-chloroanthraquinone in 5,000 parts of water containing 40 parts of caustic soda and 625 parts of sodium sulfide ($9H_2O$). The mass is heated to the boiling point and boiled for 1 to 2 hr. The amino compound is then filtered off and washed with hot water.

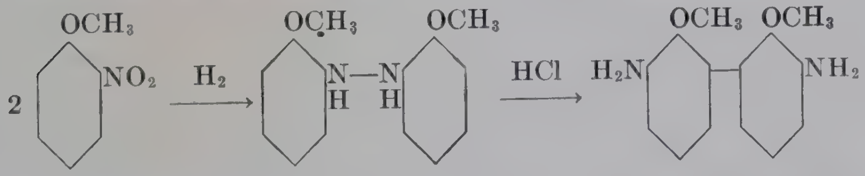
Reduction of Nitroazo Compounds.—When *p*-nitroaniline is diazotized and coupled with an amine or a phenol, a nitroazo compound is formed, thus:



Strong reducing agents will reduce not only the nitro group but the azo group as well, with the production of *p*-phenylenediamine and *p*-aminophenol. The nitroazo compound is therefore dissolved in a weak alkaline solution; and at a temperature of 40 to 50°C., 2 moles of sodium sulfide as 30 per cent crystals are slowly added. The charge is thoroughly stirred until spot tests show a change of color, thus indicating that the selective reduction is complete. The aminophenyl-azo compound is then separated by either salting out or neutralizing the solution with dilute mineral acid.

Preparation of Hydrazoanisole and Dianisidine

Reduction of *o*-Nitroanisole with Zinc in Alkaline Solution



The following process for the preparation of hydrazoanisole involves the reduction of the nitro compound in the presence of alcohol by the intermittent addition of zinc and caustic alkali, the subsequent direct distillation and recovery of the alcohol, and the extraction of the hydrazo compound from the resulting reduction mass by means of an immiscible solvent so that the hydrazo compound is obtained as a solution that is essentially free of the zinc residue which remains behind.[1]

Reduction of *o*-Nitroanisole.—One hundred fifty pounds of *o*-nitroanisole and 15 gal. of ethanol are mixed together in a steam-jacketed iron kettle provided with a reflux condenser and brought to a boil. The mixture is stirred vigorously and the reduction is effected by the intermittent and progressive addition of zinc dust and caustic soda, adding one or the other as needed at such a rate as to maintain a steady reflux, the total amount of caustic being about 16 lb. of 35 to 40°Bé. solution, and the total amount of zinc dust being about 190 lb. The amount of caustic soda corresponds to about 2 to 2.6 per cent of the theoretical amount of caustic alkali necessary to transform the zinc from the metallic state to a zincate.

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[1] U. S. 1,644,483 (1927).

The caustic soda acts as an accelerator, particularly in continuing the reaction from the azoxy to the azo stage, after which further additions of caustic have relatively little effect. The reduction can be followed to and through the azoxy and azo stages and then to the hydrazo stage (see Fig. 2). During the last stage of the reduction, the remaining zinc is added more slowly, and the reflux is maintained by means of steam delivered to the jacket of the kettle; the reduction as a whole appears to progress more slowly during this stage. It is of advantage, therefore, when the hydrazo crystals begin to separate out from test samples, to hasten the completion of the reductions by adding about 15 lb. of zinc dust in small portions at short intervals. The progress of the reaction or reduction can be followed by taking samples of the reduction mass and spotting them on paper. As the reduction nears completion, the crystals become larger, are more yellow in color, and crystallize out rapidly. They remain yellow until the reduction to hydrazoanisole is complete ,when they suddenly become almost colorless. At this stage, the mass may tend to foam somewhat, in which case the foaming may be checked by cooling of the reaction kettle. The avoidance of any large excess of zinc dust also tends to prevent excessive foaming.

After complete reduction, the mixture is of a light-gray color and relatively thick, so that the zinc oxide does not separate readily from the solution. The alcohol is then distilled off by direct heating, *e.g.*, with the steam jacket, and recovered in a highly concentrated state so that it is directly available for reuse. The direct distillation of the alcohol in this manner leaves a residue that is thick and granular and from which the hydrazoanisole can be extracted with facility by means of a solvent.

Extraction of Hydrazoanisole.—After the removal of the alcohol by distillation, the residue, consisting mainly of the hydrazoanisole with some small amounts of anisidine and of the zinc oxide residue admixed with some caustic soda or sodium zincate, is cooled to about 50°C. About 40 gal. of benzene is then added. This mixture is agitated for a period of about 1 hr. until a concentrated solution of the hydrazoanisole in benzene is obtained. It is then transferred to a settling tank; the zinc permitted to settle; and the benzene solution decanted. The zinc residue is further extracted by the addition of further amounts of benzene until all the hydrazoanisole has been extracted, leaving the zinc residue in a relatively pure state.

The total amount of benzene used may amount to 80 gal. or more. After the completion of the extraction, the remaining benzene held by the zinc residue can be recovered by distillation. The zinc oxide residue is substantially free from organic matter. By crystallization from the solvent or by distillation of the benzene, the hydrazoanisole can be obtained.

According to Weiland, it is not necessary to remove the aqueous alcohol prior to extraction of the hydrazoanisole with benzene.[1] The controlled addition of water to the reducer charge effects the coagulation and settling of the zinc oxide, thus facilitating the subsequent decantation of the benzene-alcohol solution of hydrazoanisole.

Reduction of *o*-Nitroanisole by Hydrogen; Palladium Catalyst[2]

In an iron autoclave equipped for rapid agitation are charged 100 parts of *o*-nitroanisole, 150 parts of isopropanol, 6 parts of caustic soda, and 0.015 part of palladium black supported on activated carbon. The charge is hydrogenated at 55 to 60°C. and under 100 to 200 lb. per sq. in. hydrogen pressure. The absorption of hydrogen is continued until it becomes very slow and the hydrogenated mass is then discharged from the autoclave.

Inversion to Dianisidine.—A limited quantity of water is added to the charge and the mixture is cooled to -2 to -8°C. While this temperature is maintained, 140 parts of 33 per cent hydrochloric acid is added to invert the hydrazoanisole to dianisidine hydrochloride. After the mixture has been agitated for 4 hr. at this temperature, 5 parts of iron powder is added. The agitation is continued at 0 to 10°C. until the mass becomes gray. This will require about 8 hr. Sixty parts of salt is then added, and the dianisidine hydrochloride is filtered out and washed with cold 8 per cent salt solution. The filtrate is made alkaline with lime and is then steam distilled to recover the isopropanol and *o*-anisidine. The dianisidine hydrochloride is dissolved in boiling water and is filtered at 100 to 101°C. The sludge is washed with boiling water, the filtrates being combined. The filtrate is agitated while cooling to 0 to -2°C., and the dianisidine hydrochloride which crystallizes out is filtered and washed with cold water. The filtrate and water wash, which are saturated with dianisidine hydrochloride, are saved for use in place of water in subsequent inversions. The dianisidine hydrochloride is slurried in water and is converted to dianisidine by the addition of soda ash until the slurry is alkaline. It is then cooled to 20 to 30°C., filtered, and washed with cold water. The dianisidine is dried at 90 to 100°C. under vacuum. The material is white and has a freezing point of 135.5 to 137° compared with 137° for pure material.

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[1] Weiland, U. S., 2,012,234 (1935).

[2] Henke and Benner, U. S. 2,233,130 (1941).

Reductions by Hydrogen-containing Gases: Nitrobenzene to Aniline

Previously it was indicated that an ammonia synthesis plant afforded an advantageous opportunity to obtain reducing gases ($H_2 + CO$ or $3H_2 + N_2$) for the conversion of nitro compounds to amines. In the process described in the following paragraphs, the hydrogen-nitrogen mixture is employed in conjunction with a nickel or cobalt catalyst which is suspended in the nitrobenzene-aniline stream.[1] The make-up gas $3H_2$—N_2 is used to fortify the spent gas $1H_2$—$9N_2$ which leaves the catalyst tower. Thus, about 96.3 per cent of the hydrogen entering as make-up is utilized in the hydrogenation reaction.

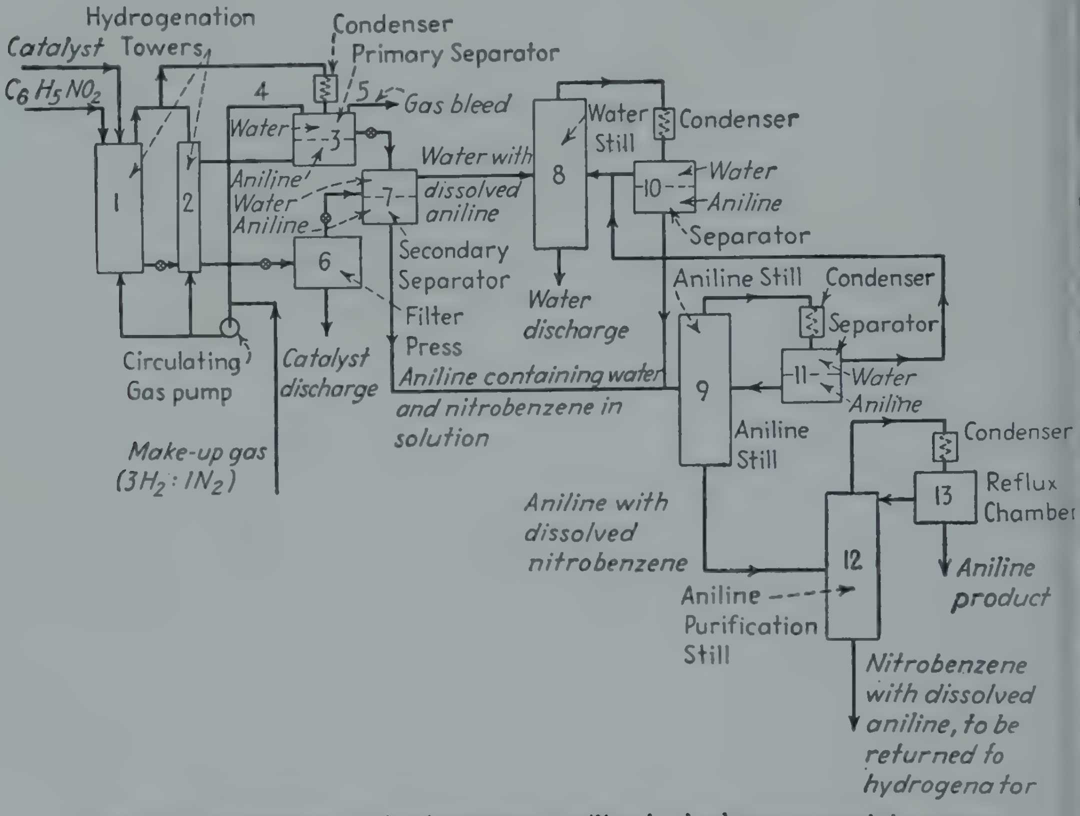
Hydrogenation
Catalyst Towers
$C_6H_5NO_2$
1
2
4
Water
3
Condenser
Primary Separator
5
Gas bleed
Aniline
Water
Aniline
7
Water with dissolved aniline
6
Secondary Separator
Filter Press
Circulating Gas pump
Catalyst discharge
Make-up gas ($3H_2$: $1N_2$)
8
Water Still
Condenser
10
Water
Aniline
Separator
Water discharge
Aniline containing water and nitrobenzene in solution
Aniline Still
Condenser
Separator
11
Water
Aniline
9
Aniline Still
Condenser
13
Reflux Chamber
Aniline with dissolved nitrobenzene
12
Aniline
Purification Still
Aniline product
Nitrobenzene with dissolved aniline, to be returned to hydrogenator

Fig. 16.—Reduction of nitrobenzene to aniline by hydrogen-containing gases.

With reference to Fig. 16, the towers 1 and 2 operating at 100° and 30 atmos. pressure are used in carrying out the reduction.[2] The make-up nitrobenzene and catalyst are introduced through separate ducts while the reducing gas containing hydrogen and nitrogen in a mole ratio of 1 : 9 is recirculated in parallel through the catalyst chambers by means of a gas pump. The recirculated gas which leaves the towers is cooled in a condenser, and the condensate is collected in the primary separator 3. The uncondensed gas is largely recirculated via line 4 to the towers, and a small portion corresponding to the make-up gas is vented through duct 5. If a relatively large volume of inert gas is used, overreduction is avoided and the problem of maintaining the solid catalyst is suspension is solved.

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[1] Kise, U. S. 2,292,879 (1942).

[2] Kise, *ibid.*

Primary hydrogenation of nitrobenzene takes place in tower 1, and the reaction mixture comprising aniline and unconverted nitrobenzene is passed to tower 2 for final reduction. Each day the contents of tower 2 are discharged to the filter press 6 to effect the separation and recovery of the catalyst. Tower 2 is refilled by using one-third the contents of tower 1, to which fresh nitrobenzene and catalyst are then added during the course of the day.

When the hydrogenation towers are operated at a temperature of about 100°C., the vapors carried out by the circulating gases are chiefly water vapor, together with a smaller amount of aniline vapor. The condensate collected in the primary separator 3 separates readily into an aqueous phase and an aniline phase. Since the mutual solubilities of water and aniline at ordinary temperatures are very low, there is no tendency to form stable emulsions. The aniline phase thus separated is returned to tower 2 for further hydrogenation; the water phase is sent to the secondary separator 7 through a pressure release valve which reduces the pressure on the liquid to about atmospheric.

Two liquid-reaction products are thus obtained in the separator 7: water containing a small quantity of aniline in solution and aniline containing a small quantity of water and unreacted nitrobenzene in solution. At 30°C., the water layer contains about 3.6 per cent by weight of aniline and the aniline layer about 5.4 per cent by weight of water, plus a small amount of nitrobenzene. A mixture of these two liquids at the boiling point is, of course, in equilibrium with a single vapor phase, *viz.*, one containing 16.5 per cent aniline and 83.5 per cent water by weight, a composition intermediate between those of the two immiscible liquids. Each of the liquid products collected in separator 7 may therefore be fractionated to remove a distillate containing about 83.5 per cent water, to leave a still residue comprising substantially pure water when the water layer is fractionated, and to obtain substantially pure aniline (together with a small quantity of unreacted nitrobenzene) when the aniline layer is fractionated.

The fractionation of the water layer is carried out continuously in still 8, and the aniline layer is continuously fractionated in the still 9. In each case, the distillate is condensed and the condensate allowed to separate into two liquid phases, the condenser and separator 10 being associated with the still 8 and the condenser and separator 11 with the still 9. The water layer from each of the separators 10 and 11, comprising about 96.4 per cent H_2O, is continuously fed to the water still 8 along with the water layer from the separator 7; the aniline layer from each of the separators 10 and 11, comprising about 94.6 per cent aniline, is continuously fed to the aniline still 9 along with the aniline layer from the separator 7. Water is continuously discharged from the still 8 and discarded, and aniline containing small amounts of unreacted nitrobenzene is continuously discharged from the still 9 and is fractionated in the still 12 to obtain a pure aniline product as a distillate which is condensed in the condenser and withdrawn from a reflux chamber 13. The residue from the still 12, a product rich in nitrobenzene, is continuously withdrawn and returned to the hydrogenator tower 1.

When the preceding methods are used, the daily output to tower 1 is as follows:

Make-up nitrobenzene	21.5 lb. moles
Nitrobenzene returned from still 12	0.11 lb. mole
Aniline accompanying nitrobenzene from still 12	0.11 lb. mole
Catalyst (a nickel-kieselguhr preparation containing 14 % Ni)	31.9 lb.

Before discharge of one-third of its contents to tower 2, the composition of the reaction mixture in tower 1 was approximately as follows:

Aniline	55.4 lb. moles
Nitrobenzene	9.76 lb. moles
Catalyst	95.7 lb.

plus a small amount of water in solution in the aniline. One-third of this reaction mixture is passed each day to tower 2 and there hydrogenated for one day. The daily material balance for tower 2 (aside from water) is as follows:

	Input	Discharge
Aniline, lb. moles	18.47	21.61
Nitrobenzene, lb. moles	3.25	0.11
Catalyst, lb	31.9	31.9

The reaction mixture discharged from tower 2, therefore, contains about 0.5 per cent unreduced nitrobenzene, and the hydrogenation load is distributed between towers 1 and 2 as 85.4 and 14.6 per cent, respectively

CHAPTER III

DIAZOTIZATION AND COUPLING

BY HAROLD E. WOODWARD

I. INTRODUCTION

Diazotization is the reaction by which a diazo compound is obtained from a primary aromatic amine. The reaction is usually carried out by treating a salt of an amine with nitrous acid in aqueous solution.

$$R{-}NH_2 + HCl + HNO_2 \rightarrow R{-}N_2Cl + 2H_2O$$

The class of diazo compounds was discovered in 1858 by J. Peter Griess. It was known at that time that an amino group on an aliphatic compound could be replaced by a hydroxyl group by treatment with nitrous acid. It had also been found that some aromatic amines could be converted into phenols in this way. Intermediate steps being omitted the reaction may be shown as follows:

$$R{-}NH_2 + HNO_2 \rightarrow R{-}OH + H_2O + N_2$$

When Griess attempted to prepare 1, 2-dihydroxy-4, 6-dinitrobenzene by the action of nitrous acid on 2-amino-4, 6-dinitrophenol (picramic acid), he obtained a new type of compound to which he gave the name *diazo*, because he believed that it contained two nitrogen atoms in place of two hydrogen atoms of the benzene ring.[1] This discovery was in a measure due to the fact that, in experimenting with picramic acid, he obtained a stable diazo oxide which is not easily decomposed. By using lower temperatures than were previously employed in this reaction, he then obtained diazo compounds from many other amines and thus opened up an important field from which many valuable commercial products have been obtained.

II. USES AND REACTIONS OF DIAZO COMPOUNDS

Among the practical uses of diazo compounds which make diazotization an important reaction are the following:

1. Some diazo compounds, being stable in the dark but decomposed in the light, are used for the preparation of light-sensitive printing papers. After exposure to light under a film, the undecomposed diazo compound is developed with a suitable solution of a compound, such as resorcinol, which combines with it to give an insoluble azo color. This type of

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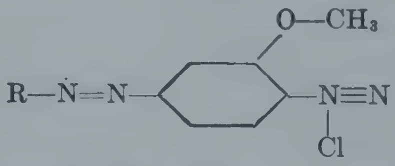
[1] GRIESS, *Ann.*, **106**, 123 (1858).

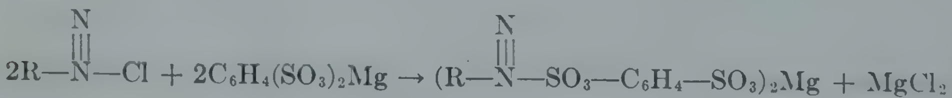
paper is used for printing from positive films, such as ink drawings, rather than from negatives, because the color is developed only under the dark part of the film where the diazo is not decomposed by the light. Four types of diazo compounds are in use for this purpose at present. They are obtained from ortho hydroxyamines, *e.g.*, 1-amino-2-naphthol-4-sulfonic acid; para tertiary aminoanilines, *e.g.*, para aminodibutylaniline; aminodiphenylamines, *e.g.*, 4-ethoxy-4′-aminodiphenylamine; and amines with ether groups, *e.g.*, 2, 5-dimethoxy-4-acetylamino-aniline.[1]

2. Many stabilized diazo compounds are produced by dyestuff manufacturers and used by dyers for dyeing or printing cotton goods that have been impregnated with a coupling component such as beta naphthol or an anilide of 2-hydroxy-3-naphthoic acid. Some of these stabilized diazo compounds are also mixed with the coupling component in an alkaline printing paste; and after this is printed on the cotton cloth, the color is developed by making it slightly acid. For example, Rapid Fast Red GL printing paste[2] is an alkaline aqueous paste consisting of a mixture of equivalent parts of the nitrosamine made from 3-nitro-4-aminotoluene and 2-hydroxy-3-naphthoic acid anilide. The azo dyes thus formed in or on the fiber are generally much less soluble in water than those which can be applied in ordinary dyeing processes, and they have unusually good fastness properties. Among the stabilized compounds in use are the following:

a. Diazonium Salts.—Some of the most stable diazonium salts may be dried and diluted with an inorganic salt to make sufficiently stable preparations. The dried diazonium sulfate obtained from *p*-nitroaniline was a commercial product before the development of the nitrosamines. Diazonium chlorides of the following type may be salted out and dried.[3]



b. Diazonium Salts of Sulfonic Acids.—These are obtained by treating a solution of a soluble diazonium salt with a solution of certain naphthalene- or benzenesulfonic acids, which form slightly soluble salts of the diazonium compound. For example, the magnesium salt of benzenedisulfonic acid may be used.[4]



$$2R-\overset{\overset{N}{|||}}{N}-Cl + 2C_6H_4(SO_3)_2Mg \rightarrow (R-\overset{\overset{N}{|||}}{N}-SO_3-C_6H_4-SO_3)_2Mg + MgCl_2$$

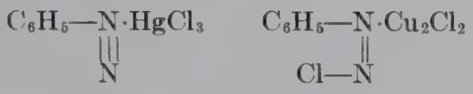
[1] **Brown**, *Chem. Ind.*, **1944,** 146.

[2] Colour Index, No. 70.

[3] Schnitzspahn, U. S. 1,846,150 (1932).

[4] Johner, U. S. 1,846,113 (1932).

c. Double Salts.—Some inorganic salts form rather insoluble addition products with diazonium salts. There are two kinds of double salts—the stable diazonium double salts, which are colorless, and the unstable *syn*-diazo double salts, which are colored.[1] They are represented by the mercuric chloride and the cuprous chloride double salts of benzenediazonium chloride.

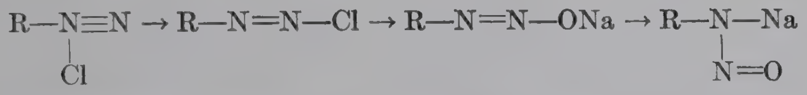


$$C_6H_5-\underset{\substack{|||\\ N}}{N}\cdot HgCl_3 \qquad C_6H_5-\underset{\substack{\|\\ Cl-N}}{N}\cdot Cu_2Cl_2$$

Zinc chloride, stannic chloride, sodium borofluoride, and cadmium chloride have been used for the preparation of stable double salts.

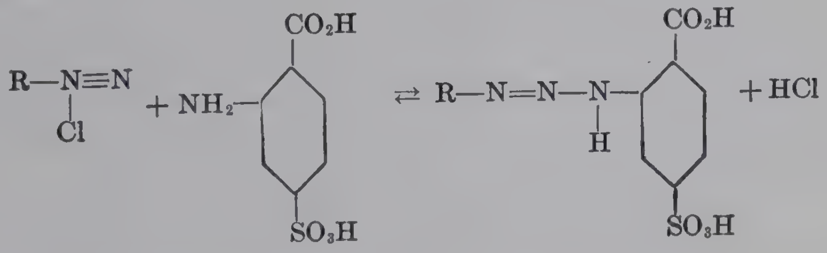
d. Nitrosamines.—These are obtained by adding a solution of a diazonium salt to a solution of sodium hydroxide. Diazonium salts containing negative groups are converted to nitrosamines at low temperatures, but others require a high temperature for the conversion. For example, *p*-nitrobenzenediazonium chloride is converted at 0°C., whereas benzenediazonium chloride requires a temperature of 130°C. Positive groups make the conversion even more difficult.

The conversion of a diazonium chloride to a nitrosamine proceeds by the following steps:



$$R-\underset{\substack{|\\ Cl}}{N}\equiv N \rightarrow R-N=N-Cl \rightarrow R-N=N-ONa \rightarrow R-\underset{\substack{|\\ N=O}}{N}-Na$$

e. Diazoamino Compounds.—These are obtained by reaction between diazonium salts and some amino compounds that do not easily couple to form azo dyes. For example, 4-sulfoanthranilic acid may be used for this purpose.[2]



The reaction goes to the right when the hydrochloric acid is neutralized with a buffer such as sodium acetate. These diazoamino compounds are stable in alkaline solution; but in acid solution the diazonium salt is regenerated.

3. The largest and most varied use of diazo compounds is for coupling with amino or hydroxy aromatic compounds to produce azo dyes, con-

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[1] HANTZSCH, *Ber.*, **28**, 1734 (1895).

[2] Hentrich, Tietze, *et al.*, U. S. 1,858,623 (1932).

taining one or more azo groups.[1] The spectral absorption curve of a simple azo dye like aminoazobenzene shows a maximum absorption at about the shortest visible wave length. Since it absorbs some violet light and transmits the rest of the visible spectrum, the color of its solution appears to be yellow. By the substitution in the benzene rings of various groups, such as hydroxyl, amino, alkyl, nitro, or sulfonic groups; by the use of naphthalene compounds instead of benzene; and by lengthening the chain of azo groups, the spectral absorption curve may be moved to longer wave lengths. The most complex azo dyes in this sense have a maximum absorption of light at about 650 mμ and are therefore green. It is thus possible, through countless variations in the structure of azo compounds, to obtain the whole range of spectral colors of different degrees of brilliance, either soluble or insoluble in water or other solvents; having affinity for a wide variety of textile fibers and other materials; and of different degrees of fastness to light, washing, and many other common destructive agents.

4. By means of a number of different reactions, the diazonium group can be replaced by certain elements or groups.[2] The most important of these reactions are the following:

a. The hydroxyl group replaces the diazonium group on heating with dilute sulfuric acid.

$$R—N_2Cl + H_2O \rightarrow R—OH + HCl + N_2$$

b. When the double salt formed with cuprous halides is heated, the diazonium group is replaced with a halogen.

$$R—N_2Cl \cdot Cu_2Cl_2 \rightarrow R—Cl + Cu_2Cl_2 + N_2$$

The same result is often obtained by using copper powder or a large excess of a halide of zinc or potassium instead of a cuprous halide.

c. A nitrile is formed when a solution of a diazonium salt is heated with potassium cyanide and copper sulfate or copper powder.

$$R—N_2Cl + KCN \rightarrow R—CN + KCl + N_2$$

d. The diazonium group is replaced with hydrogen by treatment with aliphatic alcohols in alkaline solution.

$$R—N_2Cl + C_2H_5OH \rightarrow R—H + CH_3CHO + HCl + N_2$$

The same type of reduction is obtained with metals or with hypophosphorous acid.

[1] The Colour Index lists 623 commercial azo dyes of known composition. The Census of Dyes of the U. S. Tariff Commission for the year 1940 showed the production of 55,700,000 lb. of azo dyes in this country for that year. In one color alone (Direct Black E. W.) the production for that year of 8,482,000 lb. contained about 330,000 lb. of azo nitrogen.

[2] For a complete discussion of these reactions see SAUNDERS "The Aromatic Diazo Compounds," Chap. 8, Longmans, Green and Company, New York, 1937.

e. Ethers are sometimes formed when a diazonium salt is heated with an alcohol in neutral solution.

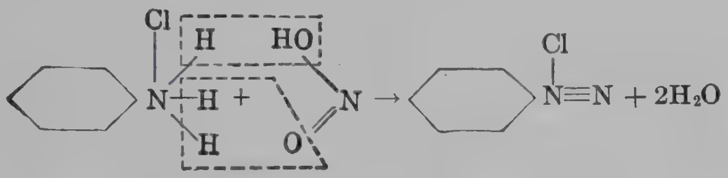
$$R—N_2Cl + CH_3OH \rightarrow R—OCH_3 + HCl + N_2$$

f. Hydrazines are obtained by reduction with potassium bisulfite.

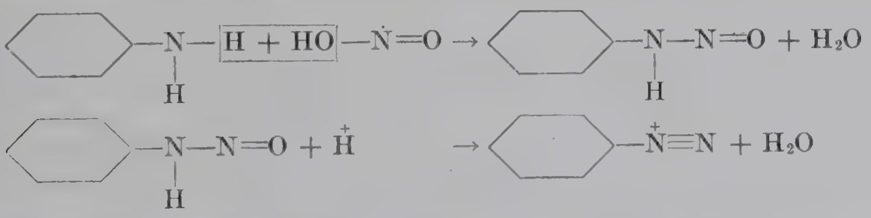
$$R—N_2Cl + 2KHSO_3 + 2H_2O \rightarrow R—NH—NH_2{\cdot}HCl + 2KHSO_4$$

III. PROPERTIES AND REACTIONS OF DIAZONIUM SALTS

The essential feature of the diazotization reaction is the replacement of three hydrogen atoms of a salt of a primary aromatic amine by one nitrogen atom. The reaction takes place between equivalent parts of a salt of the amine and nitrous acid, with the elimination of 2 molecules of water. It may be graphically represented as follows, taking aniline hydrochloride as an example:



The above formula, first proposed by Bloomstrand in 1869, and the name benzenediazonium chloride, suggested by Hantzsch in 1895, have been generally accepted as best explaining the properties of these compounds.[1] There is a possibility of the preceding reaction's taking place in two steps, and an intermediate product has been isolated in the diazotization of 1-amino-2-naphthol-4-sulfonic acid.[2] It is suggested by Conant and Tishler that a nitrosamine is first formed and this is immediately converted to the diazonium salt in acid solution.[3]



These diazonium salts are obtainable from all primary amines of the benzene and naphthalene series that do not contain in addition a hydroxyl, sulfonic, or carboxylic group. They are also obtainable in general from unsaturated isocyclic and heterocyclic compounds in which the amino group is attached to a doubly bound carbon atom of the ring.[4] There has been no published information on the formation of diazonium compounds from acyclic amines; but when such aliphatic diazonium compounds are discovered, they will probably be obtained from amines in which the amino group is attached to a doubly bound carbon atom with some other unsaturation in the compound. Among the diazotizable amino derivatives of cyclic compounds are aminoanthraquinone, -benzanthrone, -pyrene, -furane, -pyrrole, -pyridine, -pyrazole, -isooxazole, -thiazole, and -carbazole.

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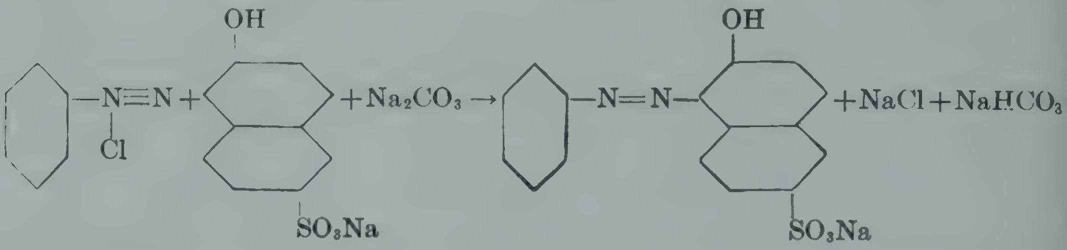
[1] Bloomstrand, *Ber.*, **8,** 51 (1875).

[2] Battegay and Schmidt, *Bull. soc. chim.*, **41,** 205 (1927).

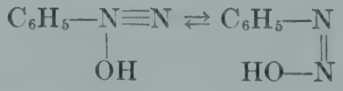
[3] Conant and Tishler "The Chemistry of Organic Compounds," p. 382, The Macmillan Company, New York, 1939.

[4] Morgan and Burgess, *Chem. News.*, **123,** 186 (1921).

The diazonium salts of hydrochloric, sulfuric, and nitric acids are very soluble in water and very reactive when treated with alkaline solutions of phenols or naphthols. For example, benzenediazonium chloride reacts rapidly with sodium 2-naphthol-6-sulfonate (Schaeffer salt) in alkaline solution to give an orange azo dye.[1]



Benzenediazonium hydroxide is a stronger base than ammonium hydroxide. As determined by saponification and by conductivity, this base is ionized about 35 per cent at 0°C. in a concentration of $N/128$. The undissociated part is in equilibrium with the weakly acid *syn*-diazo hydroxide.



$$C_6H_5-\underset{\underset{\displaystyle OH}{|}}{N}\equiv N \rightleftarrows \begin{array}{r} C_6H_5-N \\ \| \\ HO-N \end{array}$$

When treated with one equivalent of sodium hydroxide, the sodium salt is formed to the extent of 80 per cent in a concentration of $N/64$.[2] The dry salts are somewhat explosive, and in solution they decompose, especially when heated or exposed to light, with the evolution of nitrogen and the formation of a phenol, as shown on page 132. The rate of decomposition is not affected by the amount of acid in solution. At fixed temperatures and pH, the following formula applies to this decomposition reaction:

$$\frac{1}{t}\log\frac{a}{a-x} = \text{constant}$$

In this formula, t is time in minutes, a is the original amount of diazonium salt, and x is the amount of decomposed diazonium salt.

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[1] Croceine Orange, Colour Index, No. 26.

[2] DAVIDSON and HANTZSCH, *Ber.*, **31**, 1612 (1898).

When the decomposition takes place in neutral or alkaline solution, the resulting hydroxy compound sometimes couples with undecomposed diazo, thus reducing the amount of diazo compound available for further decomposition. This complicates the determination of the constant. Hodgson and Marsden have listed some of the azo compounds that they have isolated in this way.[1]

The amount of decomposition may be determined by measurement of the volume of nitrogen evolved, this being more accurate than the titration of undecomposed diazonium salt with a standard solution of a naphthol. The following values determined for this constant by Cain and Nicoll show the variation in the stability of diazonium salts at different temperatures and the effect of some substituent groups on the benzene ring:[2]

Diazotized amine	20°C.	40°C.	60°C.	80°C.	100°C.
Aniline	0.00072	0.00877	0.107		
o-Toluidine	0.00187	0.0238			
m-Toluidine	0.00208	0.0257			
p-Toluidine	....	0.0010	0.012		
p-Sulfanilic acid	....	....	0.00633	0.0709	
o-Nitroaniline	....	....	....	....	0.00546
m-Nitroaniline	....	....	....	0.00312	0.0325
p-Nitroaniline	....	....	....	0.00734	

Yamamoto determined the decomposition constant for a number of diazonium compounds and calculated the time required to decompose 1 per cent of the diazo at 0°C.[3]

DECOMPOSITION OF DIAZONIUM COMPOUNDS: 1% DECOMPOSED AT 0°C.

Diazotized Amine	Time	Diazotized Amine	Time
m-Toluidine	40 min.	2-Amino-4-nitroanisole	31 hr.
o-Toluidine	45 min.	*o*-Chloroaniline	44 hr.
Aniline	211 min.	4-Amino-3-nitrotoluene	48.5 hr.
α-Naphthylamine	460 min.	2-Amino-4-nitrotoluene	107 hr.
β-Naphthylamine	700 min.	Sulfanilic acid	158 hr.
Metanilic acid	16.5 hr.	*p*-Nitroaniline	1,053 hr.
p-Toluidine	21.5 hr.	*p*-Chloroaniline	1,294 hr.
m-Chloroaniline	25.2 hr.	*m*-Nitroaniline	1,817 hr.
o-Anisidine	25.2 hr.	*o*-Nitroaniline	3,820 days

Substituent groups which may be present on the benzene or naphthalene ring have a considerable effect on the properties of diazonium salts. Either negative groups, such as chlorine or nitro, or positive ones, such as alkoxy, increase the stability to decomposition by water. Negative groups decrease the stability to decomposition by light.[1] The rate of coupling with hydroxy or amino compounds to form azo dyes is increased by negative groups and decreased by positive groups.

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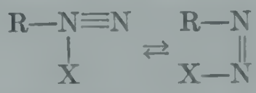
[1] HODGSON and MARSDEN, *J. Chem. Soc.*, **1943**, 378.

[2] CAIN and NICOLL, *J. Chem. Soc.*, **81**, 1412 (1902); **83**, 470 (1903).

[3] YAMAMOTO, *J. Soc. Chem. Ind. Japan*, Suppl., **36**, 59B (1933); **38**, 275B (1935).

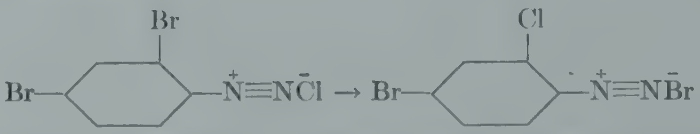
Solutions of many diazonium salts are colorless, but spectral analysis shows an absorption band in the ultraviolet.[2] The absorption band is shifted to the violet part of the spectrum in the naphthalenediazonium salts and in some substituted benzenediazonium salts, especially those containing nitro groups or substituted amino groups, so that the solutions are yellow. It has been observed that, in the dry state, diazonium iodides are more deeply colored and more explosive than the corresponding chlorides or bromides.[3] Hantzsch assumed that the dry salts consist of an equilibrium mixture of diazonium halide and *syn*-diazo halide.



$$\begin{matrix}\text{R—N}\equiv\text{N} \\ | \\ \text{X}\end{matrix} \rightleftarrows \begin{matrix}\text{R—N} \\ \| \\ \text{X—N}\end{matrix}$$

Factors that increase the proportion of diazonium salt in the dry mixtures are positive groups on R, lower temperature, and lower atomic weight of the halogen.

Some diazonium salts that contain negative groups in the aromatic nucleus are subjected to molecular rearrangement. Hantzsch observed that brominated diazonium chlorides are transformed to chlorinated diazonium bromides when bromine atoms are ortho or para to the diazonium group.[4] The transformation is more rapid at higher temperatures and in alcohol.



In many cases, a nitro, halogen, sulfonic, or methoxyl group ortho or para to a diazonium group is easily hydrolyzed in alkaline or slightly acid solution to form a diazo oxide. This is explained as being due to the strong negative character of the diazonium group, which Schoutissen found to be equal to two nitro groups in this respect.[5] The hydrolysis of the nitro group liberates nitrous acid.

IV. PROPERTIES AND REACTIONS OF DIAZONIUM SULFONATES

The reaction by which diazo compounds are obtained from aminosulfonic acids is seen to be the same as that used to explain the formation of the diazonium chlorides if we assume that, in the aminosulfonic acids, there is a salt formation between the amino group and the sulfonic group.[1] If such a formula is used for sulfanilic acid, the reaction with nitrous acid may be explained in the same way as for aniline hydrochloride.

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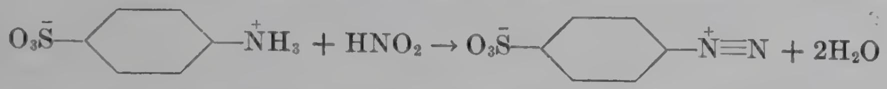
[1] Seyewetz and Mounier, *Compt. rend.*, **186**, 953 (1928).

[2] Hantzsch and Lifschits, *Ber.*, **45**, 3011 (1912).

[3] Hantzsch, *Ber.*, **33**, 2179 (1900).

[4] Hantzsch, *ibid.*, **30**, 2334 (1897); **33**, 505 (1900).

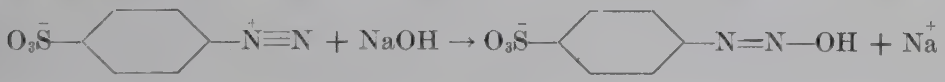
[5] Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).



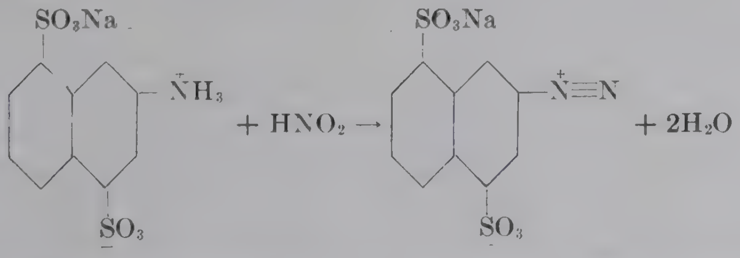
These diazonium compounds have been variously named, but they are probably best described as diazonium sulfonates, and the above compound is benzenediazonium 4-sulfonate.

The properties and reactions of the diazonium sulfonates are, in general, the same as for the diazonium chlorides, except that they are not dissociated. They are considerably less soluble, so that they may be isolated as crystalline products in fairly good yields. When the sulfonic group is ortho or para to the diazonium group, the diazonium sulfonate is rather insoluble; but when the sulfonic group is in the meta position, the diazonium sulfonate is somewhat soluble. Some of them have been reported to be explosive when dry. The color of diazonium sulfonates is the same as that of corresponding diazonium salts from unsulfonated amines.

With one equivalent of sodium hydroxide, a more soluble sodium sulfonate of a diazo hydroxide is formed. Since the diazo group is more strongly chromophoric than the diazonium group, there is a slight deepening of the color, which is confirmed by the spectral absorption value.[2]



From aniline and naphthylaminedisulfonic acids are obtained diazonium sulfonates containing a sodium sulfonate group which makes them more soluble. For example, 2-naphthylamine-4, 8-disulfonic acid, commonly known as *C acid*, reacts with nitrous acid as follows:



Aminophenol- or aminonaphtholsulfonic acids yield diazonium sulfonates except when the amino and hydroxy groups are ortho to each other. The diazonium sulfonates obtained from some aminophenolsulfonic acids have been described by Morgan and Tomlins, and the diazonium sulfonate formula has been assigned to the diazo compound of 2-amino-5-naphthol-7-sulfonic acid (J acid) by Battegay and Wolff.[1,2]

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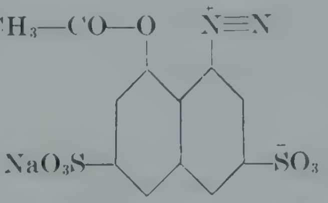
[1] SIDGWICK, "The Organic Chemistry of Nitrogen," pp. 72, 404, Oxford, Clarendon Press, 1937.

[2] HANTZSCH and LIFSCHITZ, *loc. cit.*

The hydroxynaphthalenediazonium sulfonates immediately form blue azo compounds when made alkaline. This is usually explained as a disazo color formed by coupling between two molecules.

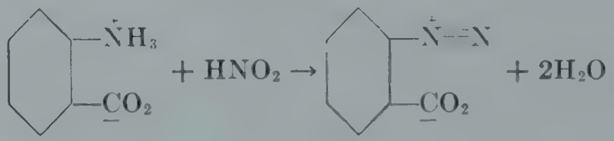
The hydroxyl group of the diazonium sulfonate obtained from 1-amino-8-naphthol-3, 6-disulfonic acid (H acid) can be acetylated to give the following compound:[3]



When this is made slightly alkaline at a low temperature, it does not immediately give a blue azo color like that obtained from the unacetylated compound.

V. PROPERTIES AND REACTIONS OF DIAZONIUM CARBOXYLATES

Aminocarboxylic acids, which do not contain in addition a hydroxyl group, yield diazo compounds similar to those obtained from aminosulfonic acids. Thus, 2-aminobenzoic acid (anthranilic acid) gives benzene-2-diazonium carboxylate when treated with nitrous acid.



Some of the aminocarboxylic acids are soluble in water as hydrochlorides; but if diazonium chlorides are formed during the reaction, they quickly change to the less soluble diazonium carboxylates. They have the same general properties as the diazonium sulfonates.

The diazonium carboxylates obtained from aminodicarboxylic acids do not usually form a soluble sodium salt of the free carboxylic group in acid solution as do the corresponding disulfonic acid derivatives. Some of the aminosulfobenzoic acids, however, give soluble diazonium sulfonates containing a sodium carboxylate group in neutral or slightly acid solution, but hydrochloric acid precipitates the free carboxylic acid.

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[1] Morgan and Tomlins, *J. Chem. Soc.*, **111**, 497 (1917).

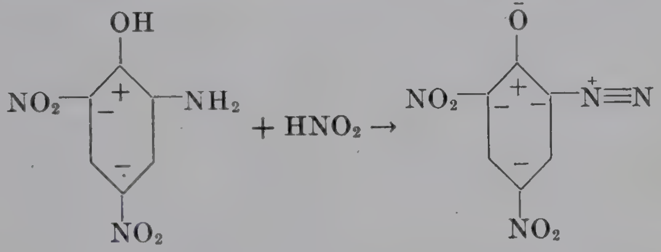
[2] Battegay and Wolff, *Bull. soc. chim.*, **33**, 1481 (1923).

[3] Jordan, Ger. 206,455 (1909).

These facts require consideration in determining the amount of acid necessary in diazotization.

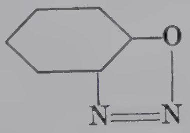
VI. PROPERTIES AND REACTIONS OF DIAZO OXIDES

Nitrous acid reacts with aminophenols and aminonaphthols to replace three hydrogen atoms with one nitrogen atom, giving a different type of diazo compounds, known as diazo oxides. For example, 4, 6-dinitrobenzene-2, 1-diazo oxide is obtained from picramic acid.



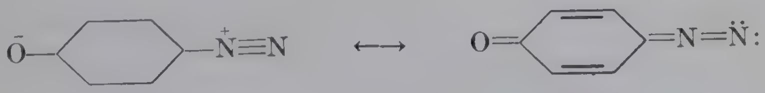
Diazo oxides are obtained from substituted aminophenols and aminonaphthols. However, diazonium sulfonates are obtained from sulfonic acids of aminophenols and aminonaphthols, except when the amino and hydroxy groups are adjacent to each other, in which case diazo oxides are obtained. Diazo oxides are obtained from aminophenolcarboxylic acids whether the amino group is ortho or para to the hydroxyl group.

In comparison with diazonium salts, the diazo oxides are more stable, more deeply colored, less soluble, and less reactive. They do not readily couple to give azo colors except in strongly alkaline solutions. It was formerly thought that these properties were best explained by the Kekulé formula



but this is an impossible structure with the Fisher-Hirschfelder atom models. The present explanation is that the induced polarization in ortho and para hydroxy diazo compounds results in a highly polarized acid hydroxyl group and a highly ionized basic diazonium group.

Resonance between the forms



may explain the properties.[1]

No diazo oxide is obtained from meta-aminophenol but only an unstable diazo salt. This may be explained as due to the induced polarization of a meta hydroxy group resulting in the transfer of the positive pole on the diazo group to the second nitrogen

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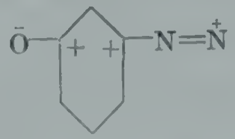
[1] Hodgson and Marsden, *J. Soc. Dyers Colourists*, **59**, 271 (1943).



The stability of the diazo oxides is well illustrated by the one obtained from 1-amino-2-naphthol-4-sulfonic acid, which is used in large amounts in the manufacture of several azo dyes. This diazo oxide may be isolated as either the free sulfonic acid or a salt (sodium, zinc, etc.) and dried or recrystallized from hot water.[1] It may be nitrated[2] or brominated.[3] It is, however, quantitatively decomposed by light.[4]

Although diazo oxides are generally rather stable, it may be noted that 4, 6-dinitrobenzene-2, 1-diazo oxide is used as a detonating explosive, being somewhat more effective than 2, 4-dinitrophenol.[5]

VII. FACTORS AFFECTING DIAZOTIZATION

Diazotization is a bimolecular reaction between equivalent quantities of un-ionized nitrous acid and a primary aromatic amine that contains an acid hydrogen. The constants of the reaction in very dilute solutions have been determined by several investigators, but the reaction is too rapid at ordinary concentrations for a determination of the constant.[6] It is agreed that the reaction proceeds very quickly at temperatures from 0 to 20°C. in concentrations of about molar to 0.2 molar, and it is probable that, under these conditions, all soluble salts of aromatic amines are diazotized at approximately the same rate. In concentrations less than 0.1 molar, the reaction is slower for amines containing alkyl or alkoxy groups but more rapid for amines containing halogen, carboxy, sulfo, or nitro groups.

Solvent.—Diazotizations are usually carried out in water solution, which is a suitable solvent in most cases. Other solvents may be used and are sometimes necessary.

When it is desired to isolate and dry the pure diazonium salts, a salt of the amine is dissolved in alcohol or glacial acetic acid and diazotized with amyl nitrite. The diazonium salts are soluble in these solvents but are precipitated by adding ether. They may also be prepared in dioxane.[1]

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[1] BATTEGAY and SCHMIDT, *loc. cit.*

[2] RUGGLI, KNAPP, *et al.*, *Helvetica Chim. Acta*, **12,** 1034 (1929).

[3] RUGGLI and MICHELS, *Helvetica Chim. Acta*, **14,** 779 (1931).

[4] SCHMIDT and MAIER, *Ber.*, **64,** 778 (1931).

[5] CLARK, *Ind. Eng. Chem.*, **25,** 663 (1933).

[6] SCHÜMANN, *Ber.*, **33,** 527 (1900); TASSILLY, *Compt. rend.*, **157,** 1148 (1913); **158,** 335, 489 (1914); TASSILLY, *Bull. soc. chim.*, **27,** 19 (1920); BOESEKEN, BRANDSMA, and SCHOUTISSEN, *Proc. Acad. Sci. Amsterdam*, **23,** 249 (1920); WILLARD, *Textile Colorist*, **46,** 22, 164 (1924); UENO and SUZUKI, *J. Soc. Chem. Ind. Japan*, Suppl., **36,** 615B (1933).

Salts of very weakly basic amines are almost completely hydrolyzed in water at low temperature and therefore cannot be diazotized in this solvent, except at high temperatures which are usually not suitable. Some such amines are soluble enough in glacial acetic acid or concentrated sulfuric acid to result in the formation of a sufficient amount of the salt to react with nitrous acid at a reasonable rate. Dimethyl formamide has also been used as a solvent for such diazotizations.[2]

Concentration.—In concentrations below $0.01M$, the reaction is rather slow; but at the usual concentrations, the reaction may be considered practically complete in 10 min. Ordinarily, the concentration of a diazonium salt at the completion of the reaction is about $0.5M$, but this may vary from a high concentration of $2\ M$ to a low concentration of $0.2\ M$. When it is impossible to avoid a greater dilution than this, a longer time up to 30 min. or even 1 hr. is allowed for the reaction to go to approximate completion.

Temperature.—The rate of the reaction is increased at higher temperatures; but since the rate is rapid at ordinary temperatures, this is not important. Generally, a temperature above 20°C. is to be avoided, because the rate of decomposition is also greatly increased at higher temperatures. However, temperatures of 30 to 60°C. are sometimes used in the diazotization of relatively insoluble weakly basic amines in order to increase the amount of salt formed in the reaction

$$\text{Amine} + \text{Acid} \rightleftarrows \text{Salt}$$

This reaction goes more completely to the right at higher temperatures; and since the formation of a salt of the amine is necessary for diazotization, elevated temperatures are sometimes employed.

The necessity for high temperatures for salt formation may often be avoided by the use of larger amounts of acid to force the above reaction to the right or by preparing the amine in a physical form that reacts more readily with dilute acids.

It is, in general, true that the amines requiring a high temperature for the formation of a salt are those whose diazonium compounds are more stable to the effect of high temperature. Oddo and Ampola and Snow have reported the possibility of obtaining satisfactory yields of some diazonium salts above 60°C.[3,4] Elevated temperatures are also necessary in the diazotization of some very insoluble monosulfonic acids of amino or aminoazo compounds from which very insoluble diazonium sulfonates are obtained.

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[1] Smith and Waring, *J. Am. Chem. Soc.*, **64**, 469 (1942).

[2] Lubs, U. S. 2,209,985 (1940).

[3] Oddo and Ampola, *Gazz. chim. ital.*, **26**, II, 541 (1897).

[4] Snow, *Ind. Eng. Chem.*, **24**, 1420 (1932).

The temperatures at which different amines may be diazotized to give the same stability as aniline diazotized at 0°C. (1 per cent decomposed in 211 min.) were calculated by Yamamoto.[1]

DIAZOTIZATION TEMPERATURE OF AMINES
DECOMPOSITION OF 1 PER CENT IN 211 MIN.

Diazotized Amine	Temp.	Diazotized Amine	Temp.
m-Toluidine	−10	Sulfanilic acid	21
o-Toluidine	−10	*m*-Nitro-*p*-toluidine	22
Aniline	0	*p*-Nitroaniline	34
Alpha-naphthylamine	4	*m*-Nitroaniline	37
Beta-naphthylamine	7	*p*-Chloroaniline	38
Metanilic acid	9	*o*-Anisidine	40
p-Toluidine	12	*o*-Chloroaniline	42
m-Chloroaniline	14	*o*-Nitroaniline	58
p-Nitro-*o*-anisidine	17		

Acid.—The function of the acid used in diazotization is threefold, as follows:

1. To supply one of the three hydrogen atoms to be replaced by nitrogen. In the case of the simple amines, this is accomplished by the formation of a salt. In the case of sodium salts of aminosulfonic acids, it is accomplished by the formation of a zwitterion. In either case, one equivalent of acid is required, but a slight excess is often necessary to reduce the hydrolytic dissociation of the salt.

Reilly and Drumm found that, without excess acid, amines diazotize at different rates depending on their basicity, and they believed that the rate is not affected by more acid than is necessary to prevent hydrolysis of the amine salt.[2] However, Schoutissen found that the influence of small amounts of hydrochloric acid is more than can be accounted for by decreasing hydrolysis.[3] This added influence of a small excess of acid is probably accounted for by the second function of acid.

2. To react with sodium nitrite and thus furnish the necessary nitrous acid. Since ionized nitrous acid does not take part in the diazotization reaction, a slight excess over the theoretical 1 mole of acid is desirable in order to repress this ionization.

3. To supply hydrogen ions sufficient to prevent reaction between the diazonium compound and any undiazotized amine in solution, as in the equation

$$R{-}N_2Cl + R{-}NH_2 \rightleftarrows R{-}N{=}N{-}NH{-}R + HCl$$

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[1] YAMAMOTO, *loc. cit.*

[2] REILLY and DRUMM, *J. Chem. Soc.*, **1935**, 871.

[3] SCHOUTISSEN, *J. Am. Chem. Soc.*, **58**, 259 (1936).

A slight excess of acid is generally enough to prevent this reaction from going to the right, except with nitro or halogenated diazonium salts, but the nitro and halogenated amines are so slightly soluble in dilute acid that this reaction is easily avoided by keeping an excess of nitrous acid in the solution. Usually, from 0.2 to 0.5 equivalent of a strong acid is a sufficient excess to take care of all these requirements, provided the amine salt is in solution.

Mineral acids are usually necessary for the complete formation of the salt and the prevention of the diazoamino coupling. Organic acids, such as acetic, are generally not suitable, unless used in considerable excess (10 to 20 moles), because the formation of the salt is incomplete, so that the diazotization is slowed up, and in such weaker acids the formation of the diazoamino compound is more rapid. Of the mineral acids, hydrochloric and sulfuric are most often used on account of their low cost. The sulfates of some amines are less soluble than the hydrochlorides, and therefore hydrochloric acid seems to be more generally suitable. As shown above, the amount of acid to be used in preparing diazonium compounds is 2.2 to 2.5 equivalents for each amino group, either in the simple amines or in the sodium salts of aminosulfonic or aminocarboxylic acids.

It has been reported that the velocity of diazotization using hydrobromic acid is about fifty times greater than when hydrochloric acid is used; and with the latter it is considerably more rapid than with nitric or sulfuric acids.[1] This difference is of practical importance only when the concentration of the diazotization is less than 0.1 *N*, as in analytical work.

In the diazotization of most aminophenols and aminonaphthols, it is not necessary to add acid for the formation of a salt, since the three hydrogen atoms to be replaced by nitrogen are already present in the amino and hydroxyl groups. Neither is acid necessary for the prevention of diazoamino coupling, for such compounds are not readily formed from aminophenols. Mineral acids are, therefore, not always used in the preparation of diazo oxides. In fact, in some cases, the use of mineral acids results in oxidation instead of diazotization.

Time.—In concentrations above 0.2 *M*, soluble amines react with almost the theoretical quantity of nitrous acid in 5 min. or less. A slight excess of nitrous acid is usually maintained for 5 to 10 min. longer. A longer time may be necessary in lower concentrations or for very insoluble amino compounds; but if a high enough temperature is used, it is not necessary to take more than 1 hr. for any diazotization.

Since the rate of decomposition of most diazonium compounds is appreciable at temperatures suitable for the diazotization, they are not kept beyond the time necessary for approximate completion of the diazotization but are used at once.

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[1] UENO and SUZUKI, *loc. cit.*

Light.—Since many diazo compounds are decomposed by light as well as by heat, it is advisable to avoid exposure to strong light. Commercial production in closed equipment is safe from this harmful action, but laboratory experiments in glass should be protected from direct sunlight.

VIII. DESIGN AND CONSTRUCTION OF EQUIPMENT

Materials of Construction.—Small laboratory preparations are, of course, made in glassware, with vacuum filtrations made on porcelain funnels. For larger amounts, enameled or stoneware containers are used. Motor-driven agitators are made of bent glass rods or wooden paddles.

In commercial-scale production, the materials used for the construction of the equipment are selected from those which withstand the action of dilute acids and in addition do not have a reducing action on diazo compounds. They include cypress, stoneware, glazed tile, rubber, enamel-lined iron, and lead. Valves of some stainless alloys are used, after being subjected to laboratory tests in solutions of diazonium salts. Lead is ordinarily the only metal used in contact with diazo compounds, as its reducing action is very slight at low temperatures.

Description of Equipment.—For commercial production on a scale of 0.2 to 2.0 pounds moles, the diazotization reaction is carried out in wooden tubs or tile-lined iron tanks of approximately equal height and diameter, which may have a capacity as high as 20,000 liters or 40,000 lb. or 5,000 gal. On the inside of the tank are several vertical ribs or baffle plates of wood or tile, projecting inward a few inches, to reduce swirling motion and improve agitation. The contents of the tub are kept in a homogeneous condition by a wooden agitator, which may be any one of several designs and is suspended in the center of the tub and geared to an electric motor in such a way that the r.p.m. may be varied from about 20 to about 40. The contents of the tank are drained through a hole at the edge of the bottom, closed on the inside with a rubber plug on a stick and on the outside by a clamp on a rubber hose or by a valve of acid-resistant metal in a lead line. The temperature of the solution in the tub may be raised by means of an open steam line of wood, lead, or rubber-covered iron reaching to the bottom. Low temperatures are attained by the addition of cracked ice. The 30 per cent solutions of the reagents are measured in calibrated tanks, those for sodium nitrite and sodium hydroxide being of iron but that for hydrochloric acid being rubber lined.

Diazotizations in concentrated sulfuric acid are made in a jacketed iron kettle with an iron agitator. The sulfuric acid solution of the diazonium sulfate is allowed to flow on to ice in one of the above-described tubs or is run directly into a solution of a coupling component.

The solution or suspension of the diazo compound is generally used directly as prepared, either in the same tub or in another similar one below it. In special cases, solutions of diazo compounds are filtered with a purified charcoal through a small wooden filter press, under pressure from a lead-lined centrifugal pump or from a lead- or tile-lined iron blow case. Sometimes, insoluble diazo compounds are purified by filtration on a wooden nutsch or a wooden filter press or by letting the crystals settle and removing the supernatant mother liquor with a syphon.

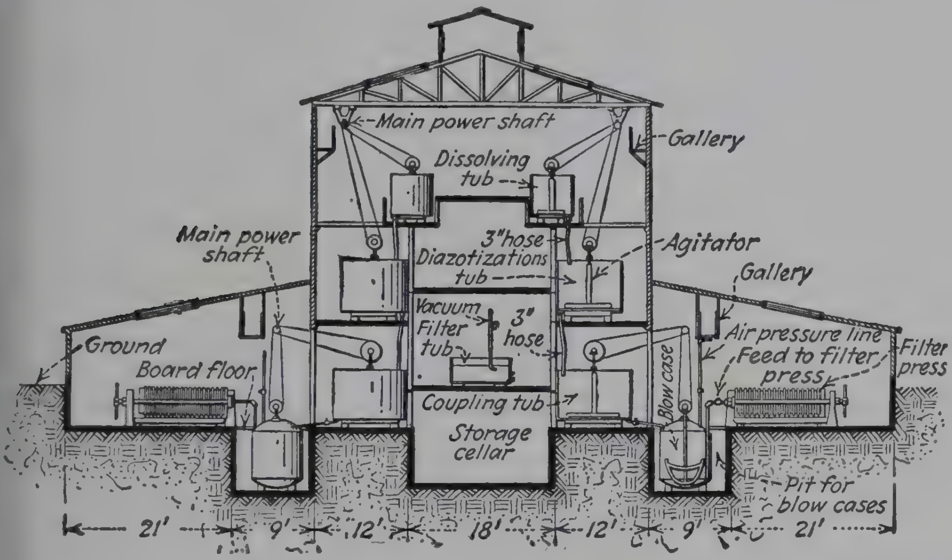

Main power shaft
Gallery
Dissolving tub
Main power shaft
3" hose
Diazotizations tub
Agitator
Gallery
Vacuum Filter tub
3" hose
Ground
Board floor
Air pressure line
Feed to filter press
Filter press
Blow case
Coupling tub
Storage cellar
Pit for blow cases
21'
9'
12'
18'
12'
9'
21'

Fig. 1.—Equipment for commercial production of diazo compounds and of azo colors. (*Courtesy of O'Brien, "Factory Practice in Manufacture of Azo Dyes."*)

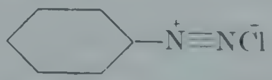
IX. TECHNICAL DIAZOTIZATIONS

Examples are given below of the usual methods of diazotization of different types of amino compounds, together with a discussion of the general application of these methods. The methods here given are for preparations of 1 mole in pounds, but any unit down to centigrams may be used equally well. Volumes are expressed in pounds, since plant equipment can be calibrated in pounds of water as easily as in gallons, and this scheme has the advantage of the metric system in making calculation of percentage concentration simpler. It also makes possible quick and accurate conversion between laboratory- and plant-scale processes, which is very valuable in maintaining a close control of plant operation.

In plant operations, cooling is usually accomplished by addition of flake ice or crushed ice and heating by use of live steam, as the slight dilution resulting from these additions is not harmful. The amount of ice to use may be roughly estimated by the formula $\frac{1.1 \text{ vol. } (T_1 - T_2)}{80 + T_2}$. For example, to cool a volume of 5,000 lb. from 30 to 5°C. requires about $\frac{5{,}500 \times 25}{80 + 5}$, or 1,618 lb. of ice. The factor 1.1 varies somewhat in different equipment, depending on its heat capacity. Since the heat of the diazotization reaction, due to the substitution of 1 atom of nitrogen for 3 atoms of hydrogen and the formation of 2 molecules of water, is about 20,000 cal., there is a rise of about 10°C. in temperature in the diazotization of a 0.5 N solution of an amine salt.[1] This requires about 250 lb. of ice for 1 pound mole of the amine to keep the temperature of the solution at 0°C. The increase in volume to be expected from the condensation of dry steam is approximately $\frac{1.1 \text{ vol. } (T_2 - T_1)}{537 + (100 - T_2)}$. For example, in raising the temperature of a charge measuring 5,000 lb. from 20 to 80°C., the volume will be increased about $\frac{5{,}500 \times 60}{537 + 20}$, or 592 lb.

The reagents used in large-scale operation are 30 per cent solutions of hydrochloric acid, sodium hydroxide, and sodium nitrite. In laboratory experimental work, a considerable amount of calculation may be avoided by using solutions made on a molar basis. Hydrochloric acid and sodium hydroxide may be used as 10 N solutions and sodium nitrite as 5 N solution in preparations of 0.1 gram mole or more. For smaller preparations, it is more convenient to use 2 N solutions; but in this case, external cooling and heating must be used to avoid dilution.

Diazotization of Simple Amines.—In 500 lb. of water, 93 lb. of aniline is dissolved as hydrochloride with 1 mole of hydrochloric acid (120 lb. of 30 per cent solution). Then 1.5 moles more acid (180 lb. of 30 per cent) is added, together with about 650 lb. of ice, this being about the amount required not only to cool all the solutions to 0°C. but also to absorb the heat of the diazotization reaction. While the solution is well agitated, 1 mole of sodium nitrite (230 lb. of 30 per cent solution) is gradually poured in, keeping the temperature below 5°C. The solution must show an acid reaction on Congo red paper, and it is tested for nitrous acid with starch-potassium iodide paper. The sodium nitrite is added until the test shows the presence of a slight excess of nitrous acid for 10 min. When there has been an excess for this length of time, the reaction is complete. A clear solution of benzenediazonium chloride is obtained, the volume of which is not over 2,000 lb.



Benzene Diazonium Chloride

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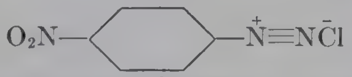
[1] Wojciechowski, *Centr.*, **106,** II, 1686 (1935).

The foregoing method is used for any amines of the benzene or naphthalene series that do not contain negative groups. In some cases, it is necessary to use a larger volume of water and a higher temperature to dissolve the salt of a base. For example, for α-naphthylamine it is necessary to use about 2,500 lb. of water at 70°C. to dissolve 143 lb. of the base as hydrochloride. If the solution of the diazonium salt is dark colored or turbid, it may be clarified by filtering with a purified charcoal, which has practically no harmful effect on the diazonium salt in a short time at a low temperature.

Diazotization of Nitroamines.—*p*-Nitroaniline is most easily diazotized if obtained as crystals that pass through a 40-mesh sieve. Larger crystals do not react completely in cold dilute acid, and very small ones dissolve too easily, so that it is difficult to avoid some diazoamino coupling during the addition of the nitrite. One hundred thirty-eight pounds of *p*-nitroaniline is stirred in 1,000 lb. of water and 300 lb. of 30 per cent hydrochloric acid at 15°C. for a few minutes until the crystals are wet. Then 230 lb. of 30 per cent sodium nitrite solution is added rapidly with good agitation. It is advisable to reserve about 2 per cent of the nitrite solution for the final adjustment. The solution is tested frequently with starch-iodide paper, and a slight excess of nitrous acid must be maintained until the reaction is complete. In case of a deficiency of nitrous acid, any undiazotized amine in solution couples to form an insoluble diazoamino compound which does not hydrolyze. The diazotization is complete in about 10 min.; and, if it is not exposed to strong light, a clear solution is obtained with a volume of about 1,500 lb. at 25°C.



p-Nitrobenzene Diazonium Chloride

Many other nitroamines may be diazotized in the same way, but those which are less soluble must be ground to a powder fine enough to pass through a 100-mesh sieve, and it may take 1 hr. to complete the reaction.

Some of the chloro- and nitroamines may be dissolved in about 5 moles of normal hydrochloric acid at 90°C.; and on rapidly cooling the solutions with ice, the bases are precipitated in a crystalline form which diazotizes easily. They may likewise be dissolved in concentrated sulfuric acid and poured into ice and water to precipitate the base. For example, 138 lb. of *p*-nitroaniline is stirred in 400 lb. of water, and 200 lb. of sulfuric acid is added. The temperature rises to about 55°C., and the base is dissolved. This solution is poured into 1,000 lb. of water and 1,000 lb. of ice with good agitation and then diazotized as above.

The dinitro- and trihalogenoamines of the benzene series, mononitro-

or halogenoamines of the naphthalene series, and the aminoanthraquinones are generally too weakly basic to be diazotized in water solutions. They may be diazotized in concentrated nitric, sulfuric, or glacial acetic acid, or suitable mixtures of these acids.

Many of these weakly basic amines may be diazotized in about 10 moles of glacial acetic acid with 2.5 moles of hydrochloric acid and 1 mole of sodium nitrite. Though the amine may not be completely dissolved in this volume of acetic acid, it is in most cases sufficiently soluble for fairly rapid diazotization. With different amines, more or less acetic acid may be required, and it may be considerably diluted in some cases.

A satisfactory method of diazotizing these weakly basic amines is with nitrosylsulfuric acid, as follows: With good agitation, 69 lb. of sodium nitrite (about 71 lb. of the commercial product) is added to 1,000 lb. of sulfuric acid (sp. gr., 1.84) at 30°C., allowing the temperature to rise to 60°C. in order to obtain a clear solution. The solution is cooled to 25°C. by external means, and 1 pound mole of the amine is added. After stirring about 1 hr., the sulfuric acid solution is poured on about 2,500 lb. of ice. The cold solution is filtered and used immediately, since groups ortho to the diazo group are gradually hydrolyzed. The large excess of sulfuric acid in the solution of the diazonium sulfate prepared in this way does not generally interfere with its use in the preparation of azo dyes, since diazonium salts containing several negative groups couple even in strongly acid solutions.

Schoutissen concluded that nitrosylsulfuric acid requires dilution in order to diazotize some amines, and he modified the above method by adding to the sulfuric acid, after the amine, two volumes of phosphoric acid (sp. gr., 1.70).[1]

Hodgson and Walker have diazotized mono- and dinitro-α-naphthylamine by dissolving in glacial acetic acid and pouring this solution into nitrosylsulfuric acid. This is probably the best method for diazotizing amines that dissolve neither in water nor in concentrated sulfuric acid.[2]

Solutions of diazonium salts of most nitroamines, by whatever method obtained, must usually be filtered with charcoal in order to obtain pure products. Water solutions of those containing two or more nitro groups are not stable on account of hydrolysis of a nitro group (see page 136). This procedure may be used for obtaining diazo oxides, as, for example, from 1-amino-2-nitro-4-halogeno (or nitro) naphthalenes.[3]

Diazotization of Aminosulfonic Acids.—A solution is prepared of 245 lb. of sodium naphthionate in 2,000 lb. of water at room temperature, and 2.5 moles of hydrochloric acid (300 lb. of 30 per cent solution) is added. The precipitated naphthionic acid is stirred for about 15 min. in order that it may become crystalline, as it will then react more rapidly. It is cooled with ice to about 12°C., and 230 lb. of a 30 per cent solution of sodium nitrite is added. A slight excess of nitrous acid is maintained for 15 min. at about 20°C., and the reaction is then practically complete. This diazonium sulfonate is light yellow in color, and it is very insoluble.

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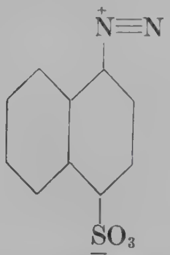
[1] Schoutissen, *J. Am. Chem. Soc.*, **55**, 4531–4534 (1933).

[2] Hodgson and Walker, *J. Chem. Soc.*, **1933**, 1620.

[3] Hodgson and Birtwell, *J. Chem. Soc.*, **1943**, 321.

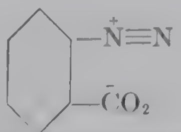


Naphthalene-1-diazonium 4-sulfonate

Other mono- or disulfonic acids of amino compounds of the benzene or naphthalene series are diazotized in a similar way. Those less soluble may be dissolved at a higher temperature; or in some cases, they may be dissolved as a more soluble salt, such as the ammonium salt. The solution is not cooled until the free sulfonic acid is precipitated, as they are obtained in a more reactive form if precipitated from solution than if the salt is allowed to crystallize before it is acidified.

In this reaction, many of the diazonium sulfonates go into solution and then crystallize out almost immediately. The insoluble sulfonates are crystalline products which may be filtered or decanted. Some of them, like that derived from 2-naphthylamine-1-sulfonic acid (Tobias acid), may be obtained in more than one crystalline form, depending on the purity of the product and modifications of the process. Although these crystalline diazo compounds can be easily isolated in fairly good yields and a high state of purity, it is rarely necessary to purify them in this way. They are not dried, as some of them are explosive.

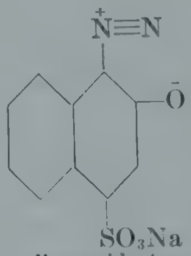
Diazotization of Aminocarboxylic Acids.—These may be treated in the same way as the aminosulfonic acids, but it is not necessary to dissolve some of them as sodium salts, as they are basic enough to form hydrochlorides. One hundred thirty-seven pounds of anthranilic acid is dissolved in 2,500 lb. of water with 1.5 moles of hydrochloric acid (180 lb. of 30 per cent). The solution is cooled to 10°C. with ice, and then 230 lb. of 30 per cent solution of sodium nitrite is added. A slight excess of nitrous acid is maintained for 10 min. at 10°C.



Benzene-2-diazonium Carboxylate

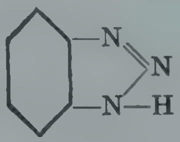
Diazotization of Aminophenols and Aminonaphthols.—No general method can be given for the preparation of the diazo oxides. Some of the aminophenols and aminonaphthols are basic enough to dissolve as hydrochlorides, and they may be diazotized like the unsubstituted amines, but 1.5 moles of acid is used instead of 2.5 moles. Some of those containing negative groups, like picramic acid, may be dissolved as the sodium or ammonium salt and treated with 2.5 moles of acid and 1 mole of sodium nitrite the same as the aminosulfonic acids. Some *o*-aminonaphthols are easily oxidized to naphthoquinones, and so they are not diazotized in acid solution. The free sulfonic acid group supplies the necessary acid in the diazotization of the important 1-amino-2-naphthol-4-sulfonic acid. A small amount of copper sulfate is used as a catalyst in this reaction. The method in general use for the diazotization of this amino compound is as follows:

A mixture of 239 lb. of 1-amino-2-naphthol-4-sulfonic acid and 1,000 lb. of water is stirred at 20°C., and a solution of 2 lb. of copper sulfate crystals in 20 lb. of water is added. Then 230 lb. of 30 per cent solution of sodium nitrite is poured in; and in a few minutes the temperature rises to about 35°C. After 15 min. more stirring, the yellow-brown solution is filtered, and either it is used directly, or the diazo oxide may be isolated. It may be precipitated as the sodium salt by adding about 300 lb. of sodium chloride or as the free sulfonic acid by adding 150 lb. of 30 per cent hydrochloric acid.



Naphthalene 1, 2-diazooxide-4-sodium Sulfonate

Diazotization of Diamino Compounds.—When some diamino compounds of the benzene or naphthalene series are treated with nitrous acid, both amino groups are diazotized; but in others, only one amino group reacts with nitrous acid. When ortho diamines are treated with nitrous acid, one amino group is diazotized, and this immediately reacts with the other amino group to form an azimino compound.[1]



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[1] LADENBURG, *Ber.*, **9**, 219 (1876).

When *m*-diamines are treated with nitrous acid, there is usually a considerable amount of coupling to produce azo dyes of the type of Bismarck brown.[1] Both amino groups of *m*-phenylenediamine may be diazotized by dissolving it together with 2 moles of sodium nitrite in water and pouring this solution gradually into 5 moles of cold $\frac{1}{2}$ *N* hydrochloric acid. Many *m*-diamines with negative substituents do not show such a tendency to couple during the diazotization, and bisdiazonium salts are more easily obtained.

The yield of the bisdiazo compound of *m*-phenylenediamine is increased by an increasing concentration of polyhydric alcohol and by an increasing number of hydroxyl groups on the polyhydric alcohol.[2]

A film apparatus has been developed that permits diazotization to proceed without coupling. In this apparatus, equivalent amounts of solutions of sodium nitrite and of *m*-phenylenediamine with excess acid are allowed to come in contact as thin films, so that the diazotization reaction takes place between relatively few molecules, and coupling with undiazotized amine is avoided.[3]

Ordinarily, only one amino group of a *p*-diamine is diazotizable, because the basicity of the second amino group is reduced so much by the diazonium group in the para position. The second amino group sometimes reacts in more concentrated acid. Schoutissen has shown that both amino groups of ortho-, meta-, and para-phenylene diamines are diazotized in concentrated sulfuric acid with nitrosyl sulfuric acid and phosphoric acid.[4]

It has been shown that phosphomolybdate, phosphotungstate, and silico tungstate salts of isomeric phenylene diamines react with 1 molecule of nitrous acid to give mono diazo compounds.[5]

Diamino compounds in which the amino groups are on different rings of diphenyl compounds such as biphenyl, dibenzyl, stilbene, diphenylamine, diphenyl ether, diphenyl urea, diphenyl sulfide, and diphenyl or triphenyl methane are generally tetrazotized without difficulty in a manner similar to that used for diazotizing monoamino compounds. Many such diamines are used for making azo dyes, and the method used for tetrazotizing dianisidine will be given as an example.

In 8,000 lb. of water, 244 lb. of dianisidine is dissolved with 240 lb. of 30 per cent hydrochloric acid at about 20°C. When solution is complete, 360 lb. of 30 per cent hydrochloric acid is added and then 460 lb. of 30 per cent sodium nitrite solution is gradually poured in during a period of about 5 min. A slight excess of nitrous acid is maintained for 10 min. at 20 to 25°C. The volume of the solution is about 9,500 lb. The solution is rather dark colored unless it is clarified with charcoal, when a yellow solution is obtained.

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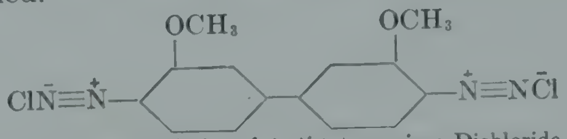
[1] Colour Index, No. 331.

[2] Kozlov and Stepanov, *J. Gen. Chem.* (USSR), **10**, 1510 (1940).

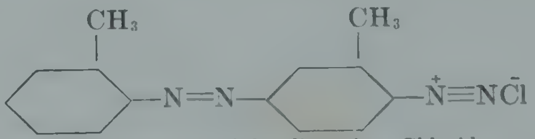
[3] Heertjes, Kolb, and Waterman, *J. Soc. Chem. Ind.*, **56**, 173 T (1937).

[4] Schoutissen, *Chem. Weekblad*, **34**, 506 (1937).

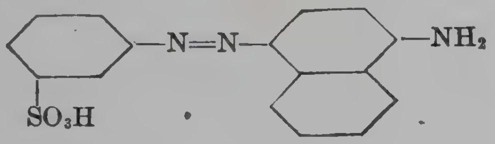
[5] Kozlov, Arkhipov, and Simanovskaya, *J. Gen. Chem.* (USSR), **10**, 697 (1940).


3.3′-Dimethoxydiphenyl-4, 4′-tetrazonium Dichloride

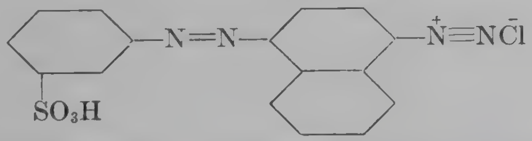
Diazotization of Aminoazo Compounds.—In the preparation of many polyazo dyes, it is necessary to diazotize a *p*-aminoazo compound, which may have been obtained by coupling a diazo compound with an amine of the benzene or naphthalene series. Those which do not contain acid groups give fairly soluble diazonium chlorides. Some of these aminoazo compounds form soluble hydrochlorides; but whether they are soluble in acid solution or not, they usually diazotize easily under about the same conditions as the simple amines, except that, on account of the lower solubility and a slower rate of reaction, the temperature should be held at 20°C. or higher. Of course, good agitation is necessary in diazotizing insoluble compounds. Aminoazotoluene may be taken as an example of this type of amine. Two hundred twenty-five pounds of aminoazotoluene is stirred in 1,000 lb. of water at 12°C. with 300 lb. of 30 per cent hydrochloric acid, and 230 lb. of 30 per cent nitrite solution is added during an interval of about 2 min. The temperature rises to about 20°C., and a slight excess of nitrous acid is maintained at this temperature for about 5 min. The solution may be clarified with charcoal at 10 to 15°C.; but at lower temperatures the diazonium chloride crystallizes out of solution.


2-Tolueneazo-3-tolyl-4-diazonium Chloride

There is such a variety of aminoazo compounds with sulfonic or carboxylic groups that they are diazotized in various ways. Some of them, with several sulfonic groups, are soluble in dilute acid and form soluble diazonium compounds. Others, with only one or two sulfonic or carboxylic groups, are more or less soluble in neutral or alkaline solution but insoluble in acid solution. These are generally prepared for diazotization by dissolving as the sodium or ammonium salt and allowing it to crystallize out, sometimes with the addition of sodium chloride. A sufficient amount of acid is then added followed by the sodium nitrite. For monosulfonic acids, a temperature above 25°C. is usually necessary; but for more soluble compounds, a temperature below 20°C. is to be preferred. The amount of acid necessary to use with the neutral sodium salts is usually 2.5 moles when there is a sulfonic group on the radical that contains the amino group and 3.5 moles when there is no sulfonic group on this radical. A diazonium sulfonate is obtained in the former case and a diazonium chloride in the latter. The reaction is usually complete in 30 to 45 min. A variation of the above general procedure is to dissolve the sodium nitrite in the neutral solution of the aminoazo compound and then add the acid to this or run it into the acid. However, this reverse method rarely offers any advantage over the ordinary direct method. The above method is illustrated by the diazotization of the aminoazo compound obtained by coupling diazotized metanilic acid with α-naphthylamine.



One pound mole of this is dissolved in 2,000 lb. of water at 20°C. with 40 lb. of sodium hydroxide. Then 3.5 moles of hydrochloric acid (430 lb. of 30 per cent solution) is added, followed by 230 lb. of 30 per cent solution of sodium nitrite, which is poured in during about 5 min. At 25 to 30°C., the nitrous acid is used up in 15 to 30 min., and enough more sodium nitrite is added to keep a slight excess for 10 min. longer at 25°C. This diazonium chloride is insoluble; and for the preparation of some dyes, it is cooled below 10°C. and filtered.



3-Sulfobenzeneazo-1-naphthalene-4-diazonium Chloride

Although the course of the reaction can generally be followed by adding the last 5 per cent of the sodium nitrite only as fast as the test with starch-iodide paper shows that it is used, it is sometimes desirable to check this observation by testing for undiazotized amine. Small amounts of many sulfonated aminomonoazo compounds can be detected by the change in color when a test portion is made alkaline and then immediately made acid on a piece of white filter paper. In alkaline solution, these compounds are yellow or orange; in acid solution, they are red or violet. In other cases, a small amount of undiazotized sulfonated aminoazo compound can be detected in a large amount of the diazo compound by adding a few drops to an alkaline solution of H acid and dipping the end of a strip of soft filter paper in it for a few minutes. The blue azo dye formed with H acid rises in the filter paper by capillary action, but the undiazotized aminoazo compound, being of lower molecular weight, rises a little higher and is easily seen.

X. ANALYSIS OF DIAZO COMPOUNDS

Methods of quantitative estimation of diazonium salts may be briefly summarized as follows:

1. Measurement of the nitrogen evolved in decomposition.

a. By hydrolysis. The acid solution or suspension of the diazonium salt is heated until the evolution of gas ceases.

b. By reduction. Nitrogen is quickly removed from diazo compounds, except diazo oxides, by treatment with *p*-phenylenediamine, and it is claimed that a determination can be made in 5 to 10 min.[1]

2. Coupling with an excess of a standard solution of a coupling component, such as β-naphthol or 1-phenyl-3-methyl-5-pyrazolone and titration of the excess with a standard solution of a diazonium salt.

3. Coupling with an excess of a coupling component and determination of the azo nitrogen by titration with standard titanium trichloride solution.

XI. COUPLING

Use of Diazo Compounds in the Manufacture of Azo Dyes.—The preparation of diazo compounds by the unit process diazotization is, for all practical purposes, a means to an important end. Diazonium compounds as a class react practically quantitatively in aqueous solution with certain amines and phenols and their derivatives. A reaction termed *coupling* takes place, and new compounds are formed containing the groups of atoms that were formerly diazo and the added *component*, united by the azo group —N=N—. The coupling process was illustrated by the formation of the dyestuff Croceine orange from benzenediazonium chloride and Schaeffer salt on page 134.

The reactants in this coupling reaction comprise on one side the class of diazo compounds and on the other side a wide variety of compounds commonly called *coupling components*. Among the coupling components commerically used are:

1. Hydroxybenzenes and naphthalenes such as phenol, cresols, resorcinol, salicyclic acid, naphthols, naphtholsulfonic acids, and hydroxynaphthoic acids. The diazo compound reacts to replace the hydrogen on the carbon ortho or para to the hydroxyl group and, in some cases, 2 or 3 molecules of a diazo couple with 1 molecule of a phenol.

2. Aminobenzenes and naphthalenes, such as *m*-toluidine, dimethylaniline, *m*-phenylenediamine, naphthylamines, and naphthylaminesulfonic acids. The amino compounds are less reactive than the hydroxy

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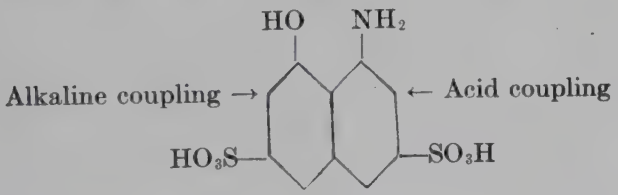
[1] Golossenko, *Chem. Zentr.*, **1937,** II, 112.

compounds and usually couple only in the position para to the amino group. Although phenol couples easily with one or more equivalents of diazo compounds, aniline scarcely couples at all but does condense in the amino group. However, N-alkyl or -dialkyl amino compounds couple more easily than the primary amines. A method of obtaining azo compounds in which aniline and other rather inactive amines are the coupling components is to form the secondary amino compounds by treating with the formaldehyde bisulfite addition compound.

$$R—NH{\cdot}CH_2SO_3Na$$

This derivative couples fairly well, and the primary amino group can then be regenerated by acid or alkaline hydrolysis.

3. Aminohydroxy compounds, such as *m*-aminophenol, aminonaphthols and aminonaphtholsulfonic acids. These coupling components couple ortho or para to the amino group in acid solution and ortho or para to the hydroxy group in alkaline solution, and some of them couple in both positions, provided the acid coupling is made first. The best known example of such a double coupling component is H acid (1-amino-8-naphthol-3, 6-disulfonic acid) from which disazo dyes are obtained.

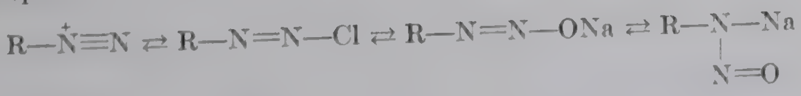


4. Beta diketo aliphatic or cyclic compounds such as aceto-acetyl aromatic amides, and barbituric acid. These compounds couple on the carbon between the keto groups, but only under conditions such that the enol form is present.[1]

5. Other components with a so-called active methylene group such as pyrazolone, especially 1-phenyl-3-methyl-5-pyrazolone.

In the azo compounds formed by the coupling reaction, the azo nitrogens are joined to carbon atoms of the diazo component and of the coupling component. Stereoisomerism is possible, but the stable form of azo compounds is the *trans* form.

Structure of the Diazo Compound.—Opinion has been divided on the question of the structure of the diazo compound that is active in the coupling reaction. This has been partly due to the lack of information on the state of the equilibrium existing between different forms of the diazo compound



$$R—\overset{+}{N}{\equiv}N \rightleftarrows R—N{=}N—Cl \rightleftarrows R—N{=}N—ONa \rightleftarrows R—\underset{\underset{\displaystyle N{=}O}{|}}{N}—Na$$

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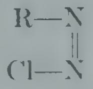
[1] Dimroth, *Ber.*, **40**, 2404 (1907).

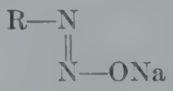
The equilibrium is affected by the character of the cyclic compound R and the groups connected to it and by the pH of the solution. The question is somewhat complicated by the fact that diazo compounds can act as bases or acids.

The most commonly accepted opinion is that the active form in coupling is the basic diazo compound R—N=N—Cl, which may correspond to Hantzsch's *syn*-diazo



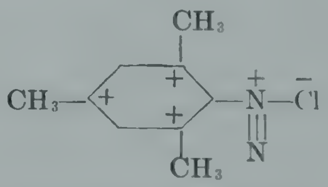
$$\begin{array}{r}\mathrm{R—N}\\ \|\\ \mathrm{Cl—N}\end{array}$$

This is in agreement with the fact that coupling is more rapid as the pH is increased but that it becomes slower at a higher pH, when the diazo compound assumes the amphoteric acid form R—N=N—ONa, which may correspond to Hantzsch's *anti*-diazotate

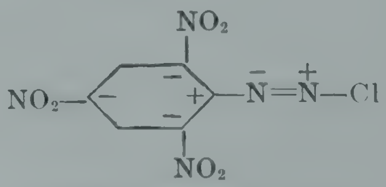


$$\begin{array}{l}\mathrm{R—N}\\ \quad\ \|\\ \quad\mathrm{N—ONa}\end{array}$$

It is supported by the principle of induced alternate polarities, for the very active diazo compounds, such as those containing nitro groups ortho and para to the diazo group, are those in which the induced positive pole is transferred to the second nitrogen atom.[1]



Does not couple in acid solution



Couples in strong acid solution

This effect of negative groups on the reactivity is shown in the following list of amines arranged in the order of increasing coupling reactivity of their diazo compounds.[2]

Increasing reactivity ↓

Aniline
2, 4, 6-Trichloraniline
3, 5-Dinitroaniline
p-Nitroaniline
2, 6-Dichloro-4-nitroaniline
2, 4-Dinitroaniline
2, 4, 6-Trinitroaniline

The most active form of diazo compound for coupling appears to be also the form that decomposes most easily, and it has been pointed out that the coupling reaction must be regarded as a race between azo compound formation and decomposition of the diazo compound.[1]

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[1] WALKER, *J. Soc. Dyers Colourists*, **39**, 293 (1923).

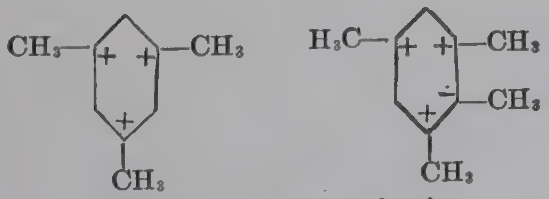
[2] SCHOUTISSEN, *J. Am. Chem. Soc.*, **55**, 4541 (1933).

Structure of the Coupling Component.—In addition to the coupling components listed above as being used commercially, many other unsaturated compounds couple to give azo compounds. Meyer found that even hydrocarbons couple, and he prepared azo compounds from 2, 3-dimethylbutadiene and *p*-nitrobenzenediazonium chloride, from isoprene and 2, 4-dinitrobenzenediazonium sulfate, and from mesitylene and 2, 4, 6-trinitrobenzenediazonium sulfate.[2]

From the studies of Meyer, in particular, it appears that the characteristic of a coupling component is that it contains a double bond between two carbons and some other conjugated unsaturation in the compound. The coupling reactivity is increased by the presence on one of the doubly bound carbon atoms of a positive or electron-repelling group, such as hydroxy; primary, secondary, or tertiary amino; ether; or methyl groups. The effect of the substituents (commonly called auxochrome groups) that increase the coupling activity is to polarize the double bond or make one of the carbons more positive than the other.

If positive groups induce a polarization that makes a compound react more easily with diazo compounds, it would be expected, according to the principle of alternate induced polarities, that additional positive groups on alternate carbons would increase the polarization and make the compound more reactive. This is actually the case, and the following examples illustrate the point:

1. The benzene hydrocarbons that have been coupled with 2, 4, 6-trinitrobenzenediazonium sulfate are those containing three methyl groups on alternate carbons, such as mesitylene, isodurene, and pentamethylbenzene, whereas other methyl substituted benzenes show little or no coupling activity.[3]



Mesitylene and Isodurene Couple

Because coupling tends to go para or ortho to existing substituents, it is clear that in the case of mesitylene, there are three positive forces making for coupling, *i.e.*, polarization with expulsion of an ortho hydrogen atom; in the case of isodurene, there is one opposing force.

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[1] Hodgson and Marsden, *J. Soc. Dyers Colourists*, **60**, 16 (1944).

[2] Meyer, *Ber.*, **52**, 1468 (1919); Meyer and Tochtermann, *Ber.*, **54**, 2283 (1921).

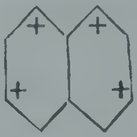
[3] Meyer, *loc. cit.*; Smith and Paden, *J. Am. Chem. Soc.*, **56**, 2169 (1934).

2. The order of coupling ability of phenols, as found by Meyer and by Goldschmidt, is[1,2]

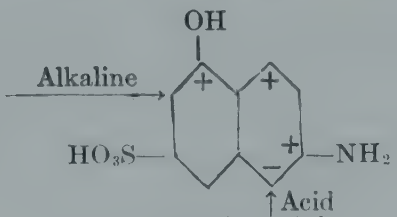
Phloroglucinol > Resorcinol > *m*-Cresol > Phenol > Hydroquinone > *o*-Nitrophenol, etc.

Here negative substituents make coupling more difficult and frequently prevent it. The coupling ability of the ethers is in the same order, but they couple much more slowly.

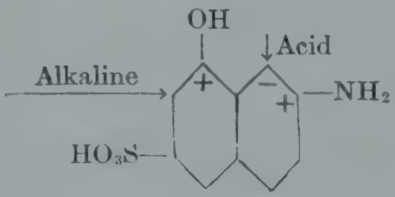
3. Among the naphthalene compounds, also, coupling takes place more easily if the hydroxy or amino groups are on alternate carbons.



This effect is most easily seen when it is attempted to couple two diazo compounds to the same coupling component. In the case of 1, 5-dihydroxynaphthalene where the effect of the hydroxy groups is opposed, it is difficult to couple a second diazo group, but 1, 6-dihydroxynaphthalene, in which the inductive effect is additive, couples easily with 2 or 3 molecules of a diazo compound.[3] In the case of 6-amino-1-naphthol-3-sulfonic acid (J acid), it is possible to couple one diazo compound in acid solution and another in alkaline solution; whereas, if 7-amino-1-naphthol-3-sulfonic acid (Gamma acid) is coupled with a diazo compound in acid solution, it does not then couple again in alkaline solution:[4]



Couples twice if coupled first in acid solution



Couples only once, either in acid or in alkaline solution

XII. MECHANISM OF THE COUPLING REACTION

It was shown above that the diazo compound is probably in the form of a *syn*-diazo hydroxide and that the coupling component has a double bond between two carbons that are polarized. Meyer believed that the coupling reaction consisted in an addition to this double bond to form

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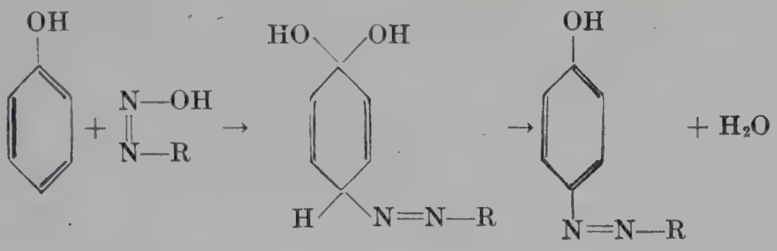
[1] MEYER, IRSCHICK, and SCHLÖSSER, *Ber.*, **47**, 1741 (1914).

[2] GOLDSCHMIDT and MERZ, *Ber.*, **30**, 670 (1897).

[3] FISCHER, *J. prakt. Chem.*, **94**, 1, 13 (1916).

[4] FIERZ-DAVID, "Kunstliche Organische Farbstoffe," p. 135, Verlag Julius Springer, Berlin, 1926.

an intermediate product from which water was eliminated to form the azo compound.[1]



The theory of an intermediate addition product is also supported by Wizinger, who obtained such addition products by coupling diazo compounds with substituted ethylene.[2] He stated that the formation of the intermediate product and the azo dye proceeds more easily the more positive the carbon atom to which the anion is added. Although such intermediate addition compounds may exist, the reaction may also be considered as the direct replacement of the hydrogen on a negatively polarized carbon atom. As stated by Hodgson, the coupling reaction may be considered as a condensation between a polarized cationoid diazo compound and an anionoid phenol or amine.[3]

XIII. FACTORS AFFECTING COUPLING

The coupling reaction is bimolecular,[4] and with the reactants in equivalent amounts the rate of reaction at constant temperature and constant pH is shown by the formula

$$k = \frac{1}{t}\,\frac{x}{a(a - x)}$$

Where k = a constant.
a = the initial concentration.
t = time in minutes.
x = concentration of reacted material.

Concentration.—From the equation, it is seen that the rate of reaction is proportional to the concentration. For reactions that are rather slow, it is therefore important to keep the concentration of reactants as near the saturation point as possible. In commercial production of azo colors, it is not always necessary to use a volume of solvent sufficient to dissolve both reactants at the temperature and pH used for the coupling, and one of them may be present as a freshly precipitated solid. It is desirable that at least one of the reactants be completely dissolved. The volume of the coupling reaction for a monazo color ordinarily is from 3,000 to 6,000 parts per mole. However, the coupling reaction is often carried out in volumes several times as great, especially in the last couplings of some polyazo colors.

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[1] MEYER, *Ber.*, **52**, 1468 (1919).

[2] WIZINGER, *Z. angew. Chem.*, 956 (1933); Brit. 435,449 (1934).

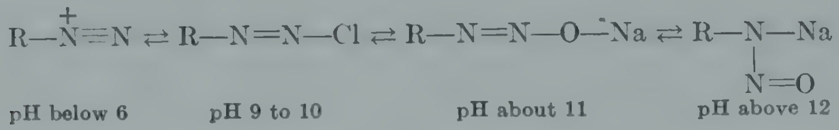
[3] HODGSON, *J. Soc. Dyers Colourists*, **58**, 228 (1942).

[4] GOLDSCHMIDT, *Ber.*, **35**, 3534 (1902); CONANT and PETERSON, *J. Am. Chem. Soc.*, **52**, 1220 (1930).

Temperature.—Raising the temperature increases the rate of coupling; but since the decomposition of diazo compounds is also more rapid at higher temperatures, couplings are usually made at low temperatures. For coupling in alkaline solution, the temperature is generally below 15°C. For couplings in acid solution, the temperature is usually above 10°C. and may be at 60°C. or higher when the coupling component is insoluble at lower temperatures.[1]

Hydrogen-ion Concentration.—Since the diazo compound is an equilibrium mixture of active and inactive forms, the concentration of active form of any particular diazo compound depends on the pH of the solution, and the rate of reaction will be greatest at the pH at which the highest ratio of active to inactive diazo exists.

As pointed out above, there is little published information regarding the range of this equilibrium for different diazo compounds. For one without positive or negative groups, the pH range of the different forms of a diazo compound has values somewhat as follows:



$$R-\overset{+}{N}\equiv N \rightleftarrows R-N=N-Cl \rightleftarrows R-N=N-O\overset{-}{-}Na \rightleftarrows R-\underset{\substack{|\\ N=O}}{N}-Na$$

Based on the conditions ordinarily used in making couplings, it appears that approximate values of the pH for maximum coupling activity in substituted benzene compounds are as follows:

Maximum Coupling Activity

Substituent	pH
Hydroxy	13
Alkyloxy	12
Alkyl	11
Unsubstituted	9
Sulfonic or halogen	7
Nitro	5
Dinitro	3

However the above values depend not only on the substituent present on the ring, but on its position relative to the diazo group. Generally a substituent has less effect in the meta position than in the ortho or para position.

In experiments with benzene diazonium chloride buffered with different metal hydroxides, Hodgson and Marsden found that the rate of decomposition relative to the rate of coupling decreases as the pH increases.[1] Their work indicates that there is an equilibrium between the coupling diazo hydroxide and the noncoupling diazotate at pH about 10.5.

---

[1] In U. S. 1,811,576 (1931), a temperature of 70 to 95°C. is used.

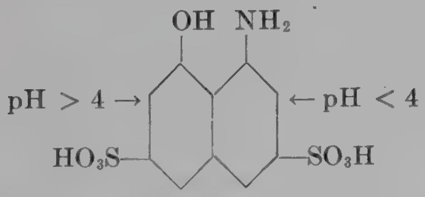
Conant and Peterson found for several couplings that

$$\log k - \log k_0 = \text{pH}$$

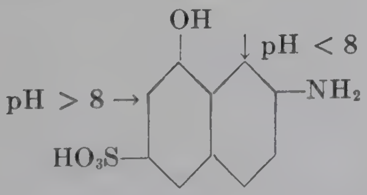
so that the coupling rate is ten times faster with an increase of one unit in pH.[2]

The hydrogen-ion concentration also affects the position of coupling in some compounds, especially those containing both amino and hydroxy groups, such as aminonaphthols. In these compounds, the amino group has the greatest effect on polarization of the conjugated double bonds in acid solution, and the coupling then takes place ortho or para to the amino group; whereas in alkaline solution, the coupling takes place ortho or para to the hydroxy group, since it is then the most effective in causing an induced polarization. The pH at which the coupling position changes varies with different aminonaphtholsulfonic acids from about pH 4 to pH 8.

For example, for H acid, the point of change is about pH 4



and for Gamma acid, it is about pH 8



Another way in which the pH influences the coupling is its effect on the solubility of the coupling component. Some naphthols, *e.g.*, 2-hydroxy-3-naphthoic acid anilide, require a high alkalinity, such as that of sodium hydroxide, for solubility in water; and at lower alkalinity, the concentration of the coupling component in solution is almost negligible at a low temperature.

The hydrogen-ion concentration is maintained in the desirable range by the use of buffer salts, such as sodium carbonate and sodium acetate.

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[1] HODGSON and MARSDEN, *J. Soc. Dyers Colourists*, **61**, 20 (1945).

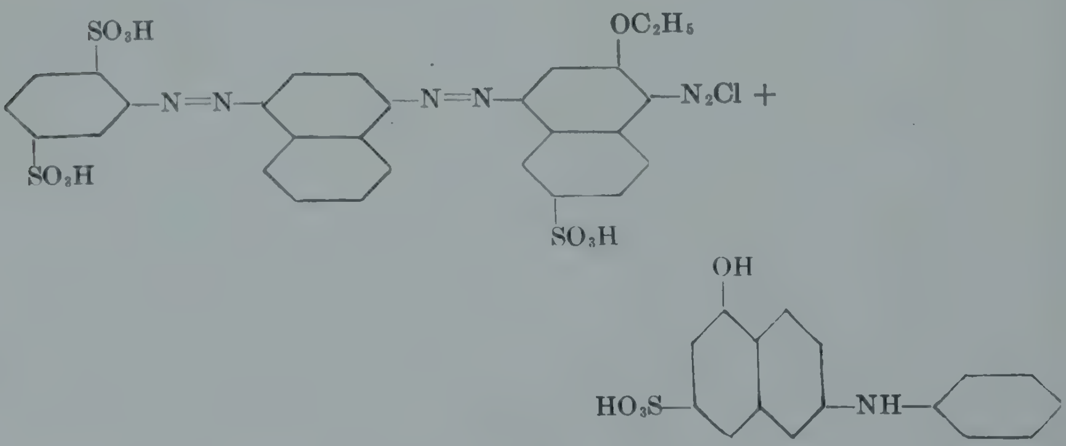
[2] *Loc. cit.*

Couplings are usually not made at a constant pH, because the diazonium compound containing an excess of acid is gradually added to the coupling component containing an excess of buffer.

Time.—From the preceding equation, it is seen that the time for completion of the reaction is inversely proportional to the concentration and the constant. Conditions of concentration and pH are usually chosen so that couplings are completed in a short time. Alkaline couplings of hydroxy compounds are generally very rapid, but acid couplings of amino compounds may take from a few minutes to several hours.

Solvent.—The diazo compounds are usually sufficiently soluble in water to allow the reaction to take place. Coupling components are also usually soluble enough; but in some cases, other solvents are required, *e.g.*, alcohol or acetic acid. Since the rate of coupling depends on the concentration of reactants in solution, it is desirable for the solvent to keep the reactants in solution or to dissolve them rapidly during the coupling. In the case of reactants of rather low solubility at the temperature or pH of the coupling, they must be precipitated or prepared in a form that dissolves easily.

In some couplings, *e.g.*,



it is necessary to use a mixture of water and pyridine as the reaction medium.[1] The use of pyridine in such cases is not because of low solubility of the reactants in water but because of a low coupling rate in water. It is not known whether the advantage in the use of pyridine is due to an increase in the polarization of the coupling component, making it more reactive, or to an effect on the form or stability of the diazo group.

Methyl alcohol may be used as a solvent for coupling amino coupling components with a diazo compound containing two or more negative groups, which is unstable in water.[2]

---

[1] Schweitzer, U. S. 1,602,991 (1926).

[2] Felix and Zuercher, U. S. 2,210,364 (1940).

The addition of glycerol to the aqueous solution is said to increase the speed of the coupling reaction.[1]

XIV. TECHNICAL COUPLINGS

Many hundreds of different coupling reactions are made on a commercial scale. They are of two main classes: those which produce marketable dyes or pigments and those made on textiles by dyers.

Azo dyes made on textile fibers are of three types:

1. Those in which the coupling component is absorbed on the fiber (usually cotton), which is then immersed in a solution of a diazonium salt. These are often called *ice colors*.

2. Those in which the amino compound or amino azo compound is absorbed on the fiber, which is then immersed in a solution of nitrous acid and later in a solution of the coupling component. These are known as *diazo colors* or *ingrain colors*.

3. Those in which a stabilized diazo compound and the coupling component are applied together as a printing paste, the printed cloth then being subjected to treatment that causes the diazo compound to become active and couple. These are the *printing colors*.

Couplings made on the fiber are complicated by the problems of application and handling of the textiles, and they will not be considered here.

Azo compounds made in substance may be classified as those in which the coupling component is a hydroxy compound, such as a phenol, a naphthol, or a keto compound (in its enol form), and those in which the coupling component is an amino compound, such as a primary, secondary, or tertiary amine.

Coupling Hydroxy Compounds in Alkaline Solution.

Chicago acid ← tolidine → Chicago acid[2]

Tolidine (212 lb.) is tetrazotized according to the method for dianisidine, described on page 152, in which the upper tub of a unit like that of Fig. 1, page 145, is used. In the lower tub, a paste is made from 716 lb. (2.1 moles) of the monosodium salt of 1-amino-8-naphthol-2, 4-disulfonic acid (Chicage acid) and 5,000 lb. of water, and solution is effected by the addition of 267 lb. of 30 per cent sodium hydroxide, the solution being tested with litmus, in order to leave the reaction still acid. The solution is cooled to 18°C. by the addition of ice; and, just before the coupling, 370 lb. (3.5 moles) of anhydrous sodium carbonate is added.

With vigorous mechanical agitation, the diazonium salt solution is run into the Chicago acid solution rather rapidly. The blue dye which separates at first gradually dissolves on further stirring. A portion of the solution is saturated with salt and tested for alkalinity on litmus paper. The salted-out sample is then poured on filter paper, and the clear rim of the spot is tested for excess Chicago acid with a solution of

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[1] KOZLOV and STEPANOV, *Chem Abs.*, **35**, 2482 (1941).

[2] This method adapted from HARTWELL and FIESER, "Organic Syntheses," vol. 16, pp. 12–17 John Wiley & Sons, Inc., New York, 1936.

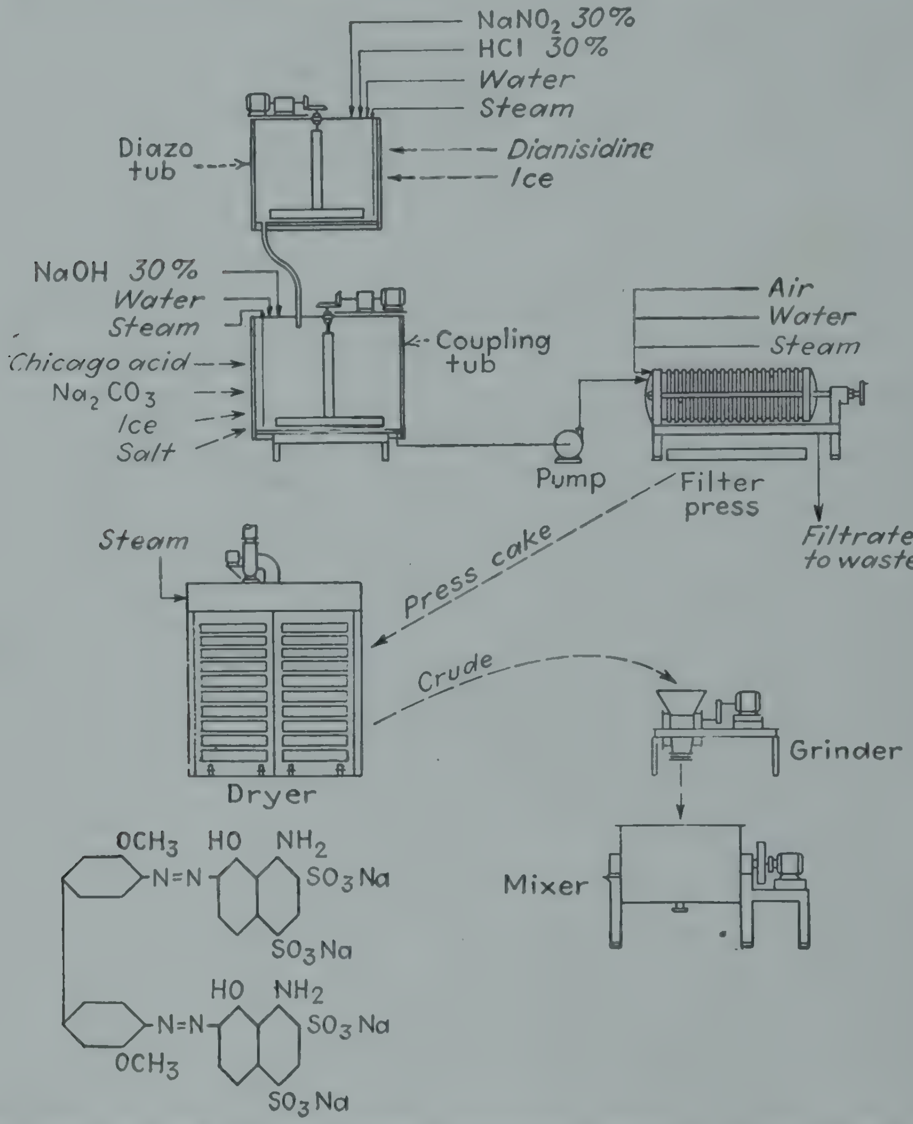
NaNO2 30%
HCl 30%
Water
Steam
Diazo tub
Dianisidine
Ice
NaOH 30%
Water
Steam
Chicago acid
Na2CO3
Ice
Salt
Coupling tub
Air
Water
Steam
Pump
Filter press
Filtrate to waste
Steam
Press cake
Crude
Grinder
Dryer
Mixer
OCH3
HO
NH2
N=N
SO3Na
SO3Na
HO
NH2
N=N
SO3Na
OCH3
SO3Na

FIG. 2. Flow sheet. Preparation of Diamine Sky Blue FF. Colour Index No. 518. Couple tetrazotized dianisidine with 2 molecular proportions of 1-amino-8-naphthol-2,4-disulfonic acid (Na salt) in alkaline solution.

diazotized sulfanilic acid. A red-violet color at the meeting of the two solutions shows the presence of Chicago acid.

After being stirred for a total of 2 hr., the mixture is heated to 85°C. and the volume estimated. For each 1,000 lb. of the solution, 250 lb. of sodium chloride (about 4,500 lb. in all) is added slowly, with vigorous stirring, in four or five portions. The dye is thus caused to separate in an easily filtrable form. When a drop of the mixture is allowed to fall on filter paper, the dye forms a dark-blue mass in the center of a violet rim. While still warm, the mixture is filtered in a plate-and-frame press with pressure from a blow case or from a centrifugal pump. The press cake (of about 40 per cent solids) is dried on pans placed in racks in an air drier, and the crude product is standardized by grinding and mixing with salt in order to equal the commercial standard which is about 25 per cent dye. Analysis shows a yield of about 85 per cent of the theoretical amount. The flow diagram for the similar preparation of Diamine sky blue FF. is shown in Fig. 2.

Couplings with most hydroxy compounds are carried out in a similar manner. The coupling component is dissolved, usually as the sodium salt, the concentration being about one-quarter normal. In order to keep the pH at a high enough value for rapid coupling, sodium carbonate was used in this example: but in some couplings, other alkalies may be used, such as ammonium hydroxide or sodium bicarbonate. The pH used for a coupling depends mainly on the coupling ability of the two reactants, but sometimes on other factors. For example, some 1-hydroxynaphthalene compounds couple in the 2 or 4 position depending on the pH. The coupling reaction is usually not carried out at constant concentration or at constant pH, since the diazonium salt with excess acid is gradually added to a solution containing the total amount of the coupling component and the buffer. The temperature of the above coupling is about as high as is used for alkaline couplings.

Coupling Hydroxy Compounds in Acid Solution.

m-Nitro-*p*-toluidine → β-naphthol[1]

m-Nitro-*p*-toluidine (152 lb.) is diazotized according to the method for *p*-nitroaniline on page 147; but since it is a weaker base, it must be ground to about 200 mesh. The solution of the diazonium chloride is filtered with charcoal and treated with some agent to remove excess nitrous acid, such as urea or sulfamic acid.[2]

In 2,000 lb. of water, 151 lb. of β-naphthol is dissolved with 143 lb. of 30 per cent sodium hydroxide solution, and 220 lb. of sodium acetate crystals is added to it. The β-naphthol is then precipitated by adding about 138 lb. of 30 per cent hydrochloric acid, or enough to make the suspension slightly acid to litmus. The clarified solution of diazonium chloride, free from excess nitrous acid, is then run into this suspension during about 45 min. at a temperature of 25 to 30°C. Testing of spots on filter paper shows the presence of β-naphthol in solution, but no excess diazo. The solution remains acid to litmus but neutral to Congo red papers. The insoluble color is filtered and washed until the wash water is no longer acid to litmus paper.

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[1] Colour Index, No. 69. For other examples of acid couplings see U. S. 921,546 (1909); 1,947,028 (1934); and 2,016,495 (1935).

[2] Lubs, U. S. 2,160,882 (1939).

This method of coupling is used for couplings of nitrodiazonium compounds with many hydroxy compounds that couple easily, such as β-naphthol and β-diketones. It is especially used for making azo compounds to be used as pigments for paints and inks to avoid the formation of slight amounts of impurities that might be formed in alkaline solution. It is necessary to avoid an excess of nitrous acid in the solution of the diazonium salt, as it would form a nitroso compound with β-naphthol. The hydroxy coupling component is first dissolved and then reprecipitated in order that it may easily dissolve as the coupling proceeds, but this step may be omitted if the coupling component is in a physical form that easily dissolves in water. When the diazonium compound contains two nitro groups (ortho or para), it couples at a low pH, and buffers are not necessary. The common buffers for acid couplings are sodium acetate and sodium formate. The temperature for acid couplings is around 20 to 30°C. Higher temperatures are used for coupling components of low solubility.

A slightly acid coupling solution is also used for coupling any diazo compound with a coupling component that easily couples more than once, as in this way the coupling may be limited to one position.

Coupling Amino Compounds in Acid Solution.

Metanilic acid → α-naphthylamine

The diazonium sulfonate is prepared from 173 lb. of aniline-*m*-sulfonic acid according to the method for naphthionic acid on page 148. There should be no excess of nitrous acid in the solution.

In 2,500 lb. of water at 75°C., 143 lb. of α-naphthylamine is dissolved as the hydrochloride with 126 lb. of 30 per cent hydrochloric acid. It is then cooled to 30°C. with about 1,200 lb. of ice. The resulting crystalline suspension is run into the diazonium sulfonate reserving about 2 per cent for the final balance. The coupling mixture, having a volume of about 8,000 lb. and a temperature of 25°C., becomes rather thick, and good agitation is required. In order to complete the coupling in a reasonable time, the mineral acidity is neutralized with 200 lb. of 30 per cent sodium hydroxide. The progress of the coupling is observed by spotting on filter paper and testing the clear rim of the spot for diazo and for coupling component. Enough α-naphthylamine is added to exactly balance the diazo and leave no excess of either component. The reaction should be complete within 1 hr. This amino azo compound may be filtered as the free acid, or it may be converted to the sodium salt and salted out. However, it is not often isolated but is diazotized and used in the production of disazo or trisazo colors.[1] The method of diazotizing it was given on page 153.

Amino compounds are usually coupled in slightly acid solution, as the amino group has more effect on the reactivity in acid solution than in alkaline solution. Since amino compounds are generally less reactive than hydroxy compounds and since they are coupled at a lower pH, higher temperatures are used.

The yield obtained in the coupling reaction is very nearly 100 per cent when the components are very reactive and the azo compound is insoluble. When the components are less active or when side reactions take place, the yield of isolated color may be 80 per cent or less.

Azo dyes made commercially are subjected to numerous tests to determine that they are equal to the standards in use. As with any colored compound, the freedom from colored and colorless impurities is best determined by means of the spectral-absorption curve of a solution of the dye. Such a curve is easily, quickly, and accurately obtained by means of an automatic recording spectrograph, and it is a specific property of a colored compound, equal in diagnostic value to any other single property or test. Individual batches of color are tested for dyeing and fastness properties, and a number of them are mixed together into a lot that may be as much as 5,000 or 10,000 lb.

Azo compounds used to color inks, paints, gasoline, and other solvents are often manufactured in a purity of about 99 per cent, but water-soluble dyes of such purity for textiles are not easily prepared, and they are generally standardized to a purity of 25 to 50 per cent with an inert material such as sodium chloride. Many water-soluble azo dyes may be prepared in a pure condition by precipitating with acid, or by the method of Lubs, which consists in repeated salting out of the color by sodium acetate and removal of the sodium acetate by extraction with alcohol.[2]

Most soluble azo compounds are easily analyzed by titration with $TiCl_3$ solution, and this method is used for a determination of the theoretical yield.[3] However, routine analysis of manufactured color is usually accomplished by a dye test or by a spectral-absorption determination of the coefficient of extinction against the standard color.

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[1] Such as Colour Index, No. 289, metanilic acid → α-naphthylamine → 1-*p*-tolylnaphthylamine-8-sulfonic acid.

[2] LUBS, *Ind. Eng. Chem.*, **11**, 456 (1919).

[3] KNECHT and HIBBERT, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Company, London, 1925.

CHAPTER IV

HALOGENATION

By P. H. Groggins and H. P. Newton

I. INTRODUCTION

Halogenation may be defined as the process whereby one or more halogen atoms are introduced into an organic compound.

The preparation of organic compounds containing fluorine, chlorine, bromine, and iodine can be accomplished by a variety of methods. The conditions and procedures differ, not only for each member of the halogen family but also with the type and structure of the compound undergoing treatment.

The chlorine derivatives, because of the greater economy in effecting their preparation, are by far the most important of the technical halogen compounds and for this reason are given primary consideration. The bromine derivative, however, sometimes has certain advantages because of the greater ease in effecting the replacement of this halogen in subsequent reactions or because it possesses certain pharmaceutical or dyeing properties.

As may be observed from the following examples, halogenations may involve reactions of (1) addition; (2) substitution, *i.e.*, of hydrogen; (3) replacement, *i.e.*, of groups, *e.g.*, the hydroxyl or sulfonic acid group.

$$HC{\equiv}CH + Br_2 \xrightarrow{\text{light}} BrHC{=}CHBr \tag{I}$$

$$CH_3COOH + Cl_2 \xrightarrow{I + P} CH_2ClCOOH + HCl \tag{II}$$

$$C_2H_5{\cdot}OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O \tag{III}$$

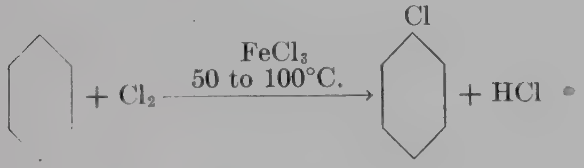
From the preceding formulations, it becomes clear that each type of reaction may involve not only a specific halogenating agent but also a suitable catalyst. The catalysts, with the exception of carbon and the activating agent actinic light, are characterized by the fact that they are halogen carriers. Thus, iron, antimony, and phosphorus, which are able to exist in two valences as halogen compounds, are used to a large extent, for they are less stable at the higher valence and give up part of their chlorine during the process. In the presence of free chlorine, such compounds alternately add on and give up halogen to carry on the reaction. Iodine and bromine, which are capable of forming mixed halogens with chlorine, are also frequently employed as catalysts in chlorinating processes.

Chlorination.—A number of methods are available for organizing the material relating to halogenation processes, all of which are necessarily complex. Here, as in other chapters, the principal classification is based on the (halogenating) agents employed. The most important methods for preparing chlorine compounds are the following:

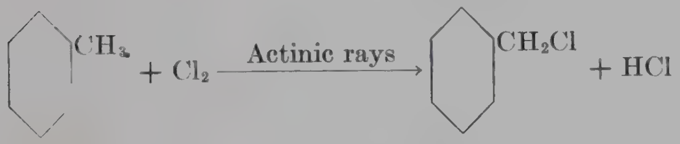
The Direct Action of Chlorine Gas.

$$H_2C{=}CH_2 + Cl_2 \xrightarrow{AlCl_3} ClH_2C{\cdot}CH_2Cl \qquad (a)$$

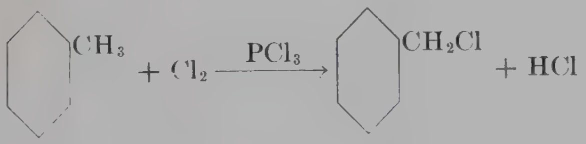
$$CH_4 + Cl_2 \xrightarrow{400 \text{ to } 500°C.} CH_3Cl + HCl \qquad (b)$$


+ Cl₂
FeCl₃
50 to 100°C.
Cl
+ HCl

(c)


CH₃
+ Cl₂
Actinic rays
CH₂Cl
+ HCl

(d)


CH₃
+ Cl₂
PCl₃
CH₂Cl
+ HCl

(e)

Hydrochloric Acid as the Chlorinating Agent.

a. Addition reaction, direct action:

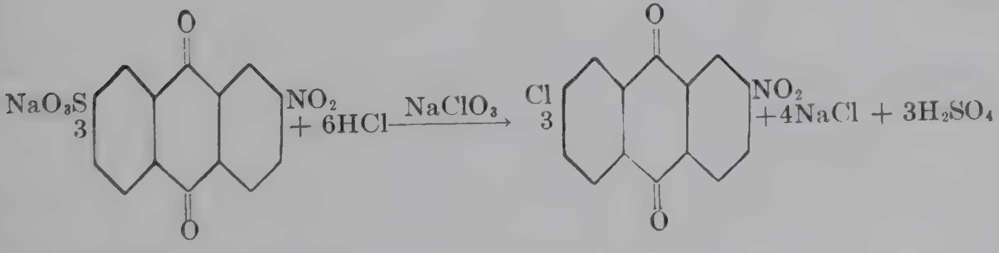
$$HC{\equiv}CH + HCl \xrightarrow{HgCl_2} H_2C{=}CHCl$$

b. Substitution reactions, indirect action:

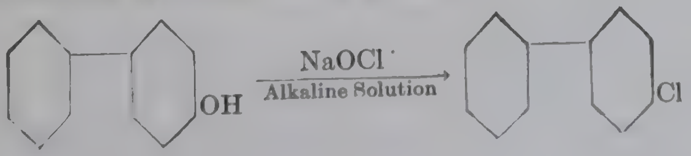
$$2C_6H_6 + 2HCl + O_2 \xrightarrow{\text{Oxidant}} 2C_6H_5Cl + 2H_2O$$

c. Replacement reactions:

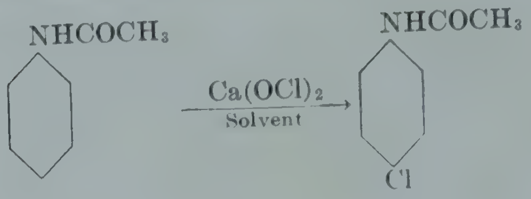
$$C_2H_5{\cdot}OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$


O
NaO₃S
3
NO₂
+ 6HCl
NaClO₃
O
Cl
3
O
NO₂
+4NaCl + 3H₂SO₄
O

Sodium Hypochlorite as Chlorinating Agent.

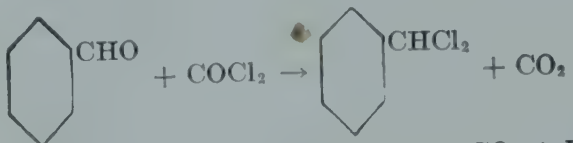

OH
NaOCl
Alkaline Solution
Cl

(a)


NHCOCH₃
Ca(OCl)₂
Solvent
NHCOCH₃
Cl

(b)

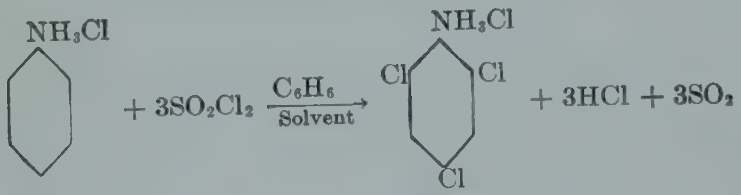
Chlorination with Phosgene ($COCl_2$).


CHO
+ COCl₂ →
CHCl₂
+ CO₂

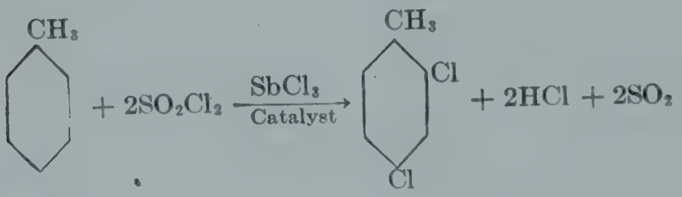
(a)

$$CH_3{\cdot}COOH + COCl_2 \rightarrow CH_3{\cdot}CO{\cdot}Cl + CO_2 + HCl \qquad (b)$$

Chlorination with Sulfuryl Chloride (SO_2Cl_2).


NH₃Cl
+ 3SO₂Cl₂
C₆H₆
Solvent
NH₃Cl
Cl
Cl
Cl
+ 3HCl + 3SO₂

(a)


CH₃
+ 2SO₂Cl₂
SbCl₃
Catalyst
CH₃
Cl
Cl
+ 2HCl + 2SO₂

(b)

Chlorination with Phosphorus Chlorides.

$$3R{\cdot}COOH + PCl_3 \rightarrow 3R{\cdot}COCl + H_3PO_3 \qquad (a)$$
$$3R{\cdot}COONa + PCl_5 \rightarrow 3R{\cdot}COCl + NaPO_3 + 2NaCl \qquad (b)$$

Preparation of Chlorine Derivatives by the Sandmeyer and Gattermann Reactions.

$$R{\cdot}N_2{\cdot}Cl + Cu_2Cl_2 \xrightarrow{HCl} R{\cdot}Cl + N_2 + Cu_2Cl_2 \quad \text{(Sandmeyer)}$$
$$R{\cdot}N_2{\cdot}Cl \xrightarrow[Cu]{HCl} R{\cdot}Cl + N_2 \quad \text{(Gattermann)}$$

Electrochemical Preparation of Halogeno Compounds.

$$C_2H_6 + Cl_2 \xrightarrow{\text{Silent electric discharge}} C_2H_5Cl + HCl$$

Bromination.—In many instances, brominations may be carried out in a manner similar to that employed for the preparation of chlorine derivatives. Thus, bromine, bromides, bromates, and alkaline hypobromites may be employed instead of the corresponding chlorine compounds. The Sandmeyer and Gatterman reactions also may advantageously be used for the preparation of bromine compounds.

Reactions involving addition and substitution are common. Bromine dissolved in water is frequently employed, particularly in the bromination of phenols. Potassium bromide is generally added to aqueous bromine solutions to increase the concentration of soluble molecular halogen. Concentrated bromine solutions are thus made available, presumably because of the following equilibrium:

$$Br_2 + KBr \rightleftarrows KBr_3$$

Bromine, hydrobromic acid, and alkali hypobromites, like the corresponding chlorine compounds, find employment in technical brominations.

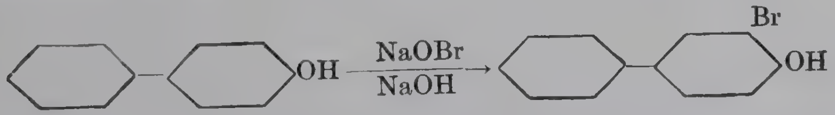
a. Addition reaction:

$$H_2C{:}CH_2 + Br_2 \rightarrow BrH_2C{\cdot}CH_2Br$$

b. Replacement reaction:

$$C_2H_5{\cdot}OH \xrightarrow[H_2SO_4]{KBr} C_2H_5Br + KHSO_4 + H_2O$$

c. Substitution reaction:



Iodination.—The methods employed in iodination differ somewhat from those for chlorination or bromination. The relatively weak C-I bond, which is indicated by the low heat of reaction and which distinguishes iodine from other halogens, makes permanent, direct union of carbon to iodine by the replacement of hydrogen possible only in exceptional cases. Such iodinations are reversible in character, as, for instance, the iodination of acetic acid:

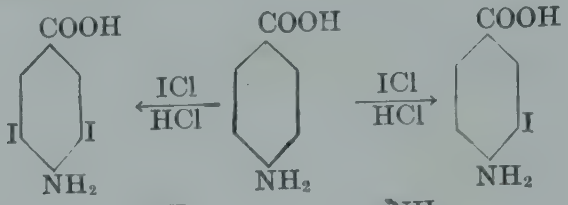
$$CH_3{\cdot}COOH + 2I \rightleftarrows CH_2ICOOH + HI$$

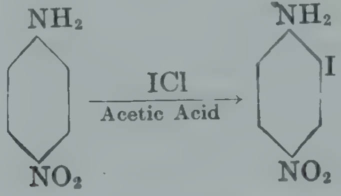
and are governed largely by the conditions employed. The hydrogen iodide tends to effect deiodination of the halogenated compounds and, indeed, is sometimes thus employed. The removal of the hydrogen iodide by such means as oxidation or absorption in alkali is consequently essential for successful iodination. When nitric acid is employed as the oxidant, practically all the iodine enters the organic compound. In the ordinary direct halogenation in the absence of an oxidizing agent, half of the reacting halogen is converted to the hydrogen halide.

Catalysts are only infrequently employed in iodination, phosphorus being the principal accelerator. Iodine monochloride,[1] because of its

$$\underset{126.92}{\mathrm{I}} + \underset{35.46}{\mathrm{Cl}} \rightleftarrows \underset{162.38}{\mathrm{I.Cl}}$$

activity under mild operating conditions is a useful catalyst for the iodination of amino compounds:





Hydriodic acid and alkali hypoiodites, like the corresponding chlorine and bromine compounds, find employment in iodinations:

$$H_2C{:}CH_2 + HI \rightarrow CH_2I{\cdot}CH_3 \qquad (a)$$

$$CH_3{\cdot}CO{\cdot}CH_3 + 3KOI \xrightarrow{\text{Alkali}} CH_3{\cdot}CO{\cdot}CI_3 + 3KOH \qquad (b1)$$

$$CH_3{\cdot}CO{\cdot}CI_3 + KOH \rightarrow CH_3{\cdot}COOK + CHI_3 \qquad (b2)$$

Fluorination.—Fluorine acts directly upon hydrocarbons to produce fluorides, but the element fluorine is troublesome to handle. The bonds holding the atoms in the fluorine molecule are stronger than in the other halogens; but once the reaction is initiated and fluorine atoms are available, they combine more readily with hydrogen and hydrocarbons than do the halogens of higher molecular weight. Furthermore, the new bonds that are formed are so strong and the heat liberated is so great that precautions must be taken to moderate the reaction so as to keep it under control. For this reason, fluorides are usually prepared by indirect methods.

1. Just as chlorine will displace bromine in hydrocarbon combinations, so fluorine will displace chlorine. The reaction is as follows:

$$RCl_n + \frac{n}{2}F_2 \rightarrow RF_n + \frac{n}{2}Cl_2$$

in which R represents the hydrocarbon radical. In the case of polychlorides, fluorine displaces the chlorine progressively, the order of displacement depending upon the structure of the polychloride. For example, trichloro-trifluorobenzene and tetrachloro-difluorobenzene have been prepared by the interaction of fluorine with hexachlorobenzene.

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[1] Prepared by passing dry chlorine gas over iodine until the increase in weight approaches the theoretical.

2. A convenient method of preparation is the reaction between sodium or potassium fluoride and alkyl hydrogen sulfate:

$$R{\cdot}H{\cdot}SO_4 + NaF \rightarrow RF + NaHSO_4$$

Methyl and ethyl fluorides may be prepared in this manner.

3. Alkyl chlorides may be made to react with silver fluoride to form the hydrocarbon fluorides:

$$RCl_n + nAgF \rightarrow RF_n + nAgCl$$

Methyl fluoride, methylene fluoride, and fluoroform may be prepared in this manner.

4. The hydrochlorides of amines may be made to react with sodium fluoride to form the organic fluorides with the elimination of ammonia:

$$R{\cdot}NH_2{\cdot}HCl + NaF \rightarrow RF + NH_3 + NaCl$$

In this manner, fluoronaphthalene may be prepared from naphthylamine.

5. The polychlorinated alkanes will react with hydrogen fluoride in the presence of antimony pentachloride.

$$\begin{aligned} CCl_4 + 2HF &\rightarrow CCl_2F_2 + 2HCl \\ C_2H_2Cl_4 + 2HF &\rightarrow C_2H_2Cl_2F_2 + 2HCl \\ CCl_3F + HF &\rightarrow CCl_2F_2 + HCl \end{aligned}$$

Other chlorinated and brominated acylic compounds, such as hexachloroethane, trichloroethylene, ethylene dibromide, tetrabromobutane, and bromoform, can be used for the preparation of the corresponding fluorine derivatives.

6. Diazo compounds react with hydrogen fluoride and borontrifluoride to form organic fluorides with the liberation of nitrogen:

$$R{\cdot}N{:}N{\cdot}Cl + HF \rightarrow RF + N_2 + HCl$$

3, 4-Dichlorofluorobenzene has been prepared by diazotizing the sulfate of 3, 4-dichloroaniline and digesting the diazonium sulfate with hydrofluoric acid.

7. Tetraalkylammonium fluorides may be heated to produce alkyl fluorides and tertiary amines:

$$R_4{\cdot}N{\cdot}F{\cdot} \xrightarrow{\text{Heat}} RF + N{\cdot}R_3$$

8. Acetyl fluoride may be prepared by reacting acetic acid with phosphorus trifluoride:

$$3CH_3{\cdot}COOH + 2PF_3 \rightarrow 3CH_3{\cdot}COF + P_2O_3 + 3HF$$

9. Acetyl fluoride will react with benzaldehyde to form triphenyl fluoromethane:

$$3C_6H_5{\cdot}CHO + CH_3{\cdot}COF \rightarrow C{\cdot}(C_6H_5)_3F + C_2H_4(COOH)_2$$

Hydrogen fluoride does not possess the capacity to form addition compound with unsaturated hydrocarbons, a characteristic that becomes more pronounced with increased molecular weight and diminished heat of formation of the hydrogen halide. This is to be expected, since the high dielectric constant indicates that liquid hydrogen fluoride consists of long chains of molecules in which the bond between H and F in $(HF)x$ is very strong. The formation of hydrogen fluoride salts of amines, which contain 4 molecules of HF attached to the base, *e.g.*, $R{\cdot}NH_2(HF)_4$, is evidence of such a high state of association. Furthermore, vapor-pressure measurements and vapor-density determinations can be explained only on the basis of an equilibrium

$$6HF \rightleftarrows (HF)_6$$

II. THEORY OF HALOGENATION REACTIONS

By Raymond H. Ewell[1]

Many reactions of halogens with organic compounds are recorded in the literature, and some of them are utilized in commercial processes. The great variety of results reported for a wide variety of conditions precludes a complete, clear interpretation of these phenomena, but an analysis of some of the results and application of some theoretical considerations will throw light in the subject.

In order to analyze experimental results on chemical reactions, a clear separation of *equilibrium* and *reaction-rate effects* must be made. Sometimes equilibrium determines the product observed, and sometimes rate of reaction does. In the consideration of both equilibrium and reaction rates, reference to the "bond energies" of the chemical bonds involved is frequently helpful, and some pertinent bond energies are given in Table I. The heat of a reaction is given approximately by the sum of the energies of the bonds formed minus the sum of the energies of the bonds broken. The ΔH of reaction is the negative of this.

Thermodynamics of Halogenation Reactions[2]

Substitution Halogenation.—A survey of the thermodynamics of substitution halogenation reactions shows that ΔH is highly exothermic in the case of Cl, moderately exothermic for Br, and endothermic for I and that ΔS° is very small in all cases. ΔF° is therefore negative, and the equilibrium is in favor of the right-hand side of the reaction at all temperatures for Cl and Br; but ΔF° is positive, and the equilibrium is in favor of the left-hand side of the reaction at all temperatures for I. These deductions are illustrated by data on the following reactions at 25°C., in which all reactants and products are in the gaseous state at 1 atmos. pressure;

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[1] Research chemist, Shell Chemical Corp.

[2] The symbols used here are in accord with Lewis and Randall, *loc. cit.*, where ΔH = change in heat content; ΔS = change in entropy and ΔF = change in free energy. Superscript zeros refer to standard state of gas at 1 atmos. pressure.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	$\Delta H = -23{,}900$ cal.
	$\Delta S^\circ = +2.84$ cal./mole deg.
$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$	$\Delta H = -23{,}700$ cal.
	$\Delta S^\circ = +0.04$ cal./mole deg.
$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$	$\Delta H = -24{,}000$ cal.
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	$\Delta H = -24{,}400$ cal.
$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$	$\Delta H = -26{,}700$ cal.
	$\Delta S^\circ = +3.57$ cal./mole deg.
$C_2H_5Cl + Cl_2 \rightarrow CH_2Cl{\cdot}CH_2Cl + HCl$	$\Delta H = -25{,}700$ cal.
$CHCl_2{\cdot}CHCl_2 + Cl_2 \rightarrow C_2HCl_5 + HCl$	$\Delta H = -24{,}100$ cal.
$C_2H_4 + Cl_2 \rightarrow C_2H_3Cl + HCl$	$\Delta H = -24{,}800$ cal.
$C_2HCl_3 + Cl_2 \rightarrow C_2Cl_4 + HCl$	$\Delta H = -23{,}100$ cal.
$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$	$\Delta H = -23{,}100$ cal.
$CH_4 + Br_2 \rightarrow CH_3Br + HBr$	$\Delta H = -6{,}500$ cal.
$CH_4 + I_2 \rightarrow CH_3I + HI$	$\Delta H = +10{,}400$ cal.

It will be noted that ΔH of chlorination is in the range of $-23{,}000$ to $-27{,}000$ cal. regardless of the nature of the rest of the molecule containing the hydrogen atom being substituted. Since the heats of formation of chloro compounds are usually not very accurate, it is possible that the few cases outside the range of $-23{,}000$ to $-25{,}000$ cal. are due to inaccurate data. If the bond energies in Table I are used, the heat of substitution chlorination is calculated as $-24{,}000$ cal. The agreement of this figure with the experimental heats of reaction leads to the expectation

Table I.—Bond Energies at 25°C. in Kilocalories

Type of bond	F	Cl	Br	I
X—X	63.5	57.8	46.1	36.3
H—X	147.6	102.9	87.4	71.6
C—X	103.8	66.6	53.0	38.7
C—C	56.2		I—Br	42.9
C═C	95.8		I—Cl	51.0
C≡C	124.5		Br—Cl	52.7
C—H	87.7		Cl—F	86.4
H—H	103.8			

that the heat of substitution chlorination would be in this range for all organic molecules and that it should also be true for reactions in the liquid state as well as in the gaseous state.

Since there is no change in the number of molecules in all the above reactions, $\Delta S°$ is very small, and $T\Delta S°$ is negligibly small compared with ΔH. Therefore $\Delta F°$ can be taken as approximately equal to ΔH, according to the general relation $\Delta F° = \Delta H - T\Delta S°$. This means that in all substitution chlorination reactions, equilibrium is overwhelmingly in favor of the chlorinated product at all temperatures. The same will be true for bromination reactions. However, for iodination, ΔH and $\Delta F°$ are both positive and equilibrium is in the opposite direction at all temperatures.

Addition Halogenation.—A survey of the thermodynamics of the addition of halogens to double bonds shows that ΔH is highly exothermic for all the halogens and $\Delta S°$ is of the order of −30 cal. per mole deg., since there is a change of negative one in the number of molecules. $\Delta F°$ is therefore negative, and equilibrium is in favor of the right-hand side of the reaction at all temperatures up to about 1000°C. for Cl, up to about 700°C. for Br, and up to about 50°C. for I. These conclusions are illustrated by the following reactions, in which the data are for the same conditions as given above:

$C_2H_4 + Cl_2 \rightarrow CH_2Cl{\cdot}CH_2Cl$ $\Delta H = -41{,}000$ cal.
$\Delta S° = -27.5$ cal./mole deg.
$C_2HCl_3 + Cl_2 \rightarrow C_2HCl_5$ $\Delta H = -44{,}000$ cal.
$C_2H_4 + Br_2 \rightarrow CH_2Br{\cdot}CH_2Br$ $\Delta H = -30{,}000$ cal.
$C_2H_4 + I_2 \rightarrow CH_2I{\cdot}CH_2I$ $\Delta H = -9{,}600$ cal.

Hydrohalogenation-dehydrohalogenation.—A survey of the thermodynamics of this type of reaction shows that ΔH is highly endothermic in all cases (for the dehydrohalogenation direction as written below) and $\Delta S°$ is of the order of +30 cal. per mole deg., since there is a change of positive one in the number of molecules. $\Delta F°$ is therefore negative, and equilibrium is in favor of dehydrohalogenation at all temperatures above about 250°C. for Cl and above about 200°C. for Br and I. These deductions are illustrated by the following reactions in which the data are for the same conditions as given above:

$C_2H_5Cl \rightarrow C_2H_4 + HCl$ $\Delta H = +15{,}300$ cal.
$\Delta S° = +31.3$ cal./mole deg.
$CH_2Cl{\cdot}CH_2Cl \rightarrow C_2H_3Cl + HCl$ $\Delta H = +16{,}200$ cal.
$C_2H_5Br \rightarrow C_2H_4 + HBr$ $\Delta H = +14{,}200$ cal.
$C_2H_5I \rightarrow C_2H_4 + HI$ $\Delta H = +14{,}000$ cal.

This equilibrium is quite important in determining the results of chlorination, particularly since chlorine is a powerful homogeneous catalyst for the dehydrochlorination reaction. Some experimental results on chlorination of ethylene and vinyl chloride given in a later section agree with this equilibrium picture. This discussion has not included reactions for the type $C_2H_3Cl \rightarrow C_2H_2 + HCl$, which would probably have quite different thermodynamics, since triple bonds are involved.

MECHANISMS AND RATES OF HALOGENATION REACTIONS

The rate of a chemical reaction is determined primarily by the magnitude of the activation energy. This quantity is related to the rate of reaction by the relations

$$k = se - {}^{-A/RT}$$

or

$$d\ln k/dT = A/RT^2$$

where k is the specific reaction rate constant, A is the activation energy, and s is a proportionality constant which has only a small temperature variation. The lower the magnitude of A the faster a reaction will be. Owing to the exponential effect, one reaction will predominate over another if its activation energy is only 1 kg. cal. lower than that of a competing reaction, provided their s factors are of comparable magnitude.

A is a complex function of the energies of bonds broken and formed in the reaction, so that, for most reactions, A is an experimental quantity only. However, in reactions in which one of the reactants is a free atom or a free radical, A can be estimated approximately from bond energies. Furthermore, A can be calculated for some more complex reactions by the methods of quantum mechanics, but the method is very laborious, and the results subject to considerable error due to necessarily rough approximations.

The mechanisms and rates discussed in this section apply primarily to homogeneous, noncatalytic, thermal, gas-phase reactions. However, the effect of homogeneous and heterogeneous catalysts and of irradiation will be mentioned in some cases. Many of the ideas discussed apply also to liquid-phase reactions, depending on the solvent.

The reactions of halogens with organic compounds, especially hydrocarbons, have some analogies to the simpler reactions of halogens with hydrogen, which will therefore be discussed briefly first.

Reactions of the Halogens with Hydrogen.—Two possible mechanisms suggest themselves:

$$\text{I.}\quad H_2 + X_2 \rightarrow 2HX \qquad (1)$$

$$\text{II.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (2) \\ X + H_2 \rightarrow HX + H & (3) \\ H + X_2 \rightarrow HX + X & (4) \\ \text{etc., etc.} & \end{cases}$$

Mechanism I involves simply bimolecular collisions between the two species of reacting molecules. Mechanism II is a chain reaction initiated by halogen atoms from partial dissociation of halogen molecules. The activation energy of mechanism I can be calculated only by laborious methods of quantum mechanics or determined experimentally in case that is the actual mechanism of the reaction. The over-all activation energy of mechanism II is given by the heat absorbed by reaction (2) plus the activation energy of reaction (3). The activation energy of atomic reactions, such as (3) and (4), is nearly zero if the reaction is exothermic and is approximately equal to the heat of reaction if the reaction is endothermic. The required heat of reaction can be estimated from the difference in bond energies of bonds formed and broken. Reaction (4) does not enter into the calculation of the activation energy, since such reactions involving atomic hydrogen are always exothermic and therefore fast.

Table II gives some activation energies calculated by quantum mechanics by Eyring for the bimolecular reactions (except iodine) and by the bond energy method for the atomic reactions of type (3).[1] These calculated activation energies are in good accord with experimental evidence. Table II predicts that the reactions of F, Cl, and Br with hydrogen will be chain reactions rather than bimolecular reactions, whereas the reaction with I will be a bimolecular reaction. These are known to be true from the kinetic equations found experimentally for these reactions and from the effect of surfaces and of oxygen on the reactions with Cl and Br. Morris and Pease have deduced from experimental data activation energies of 6.0, 17.7, and 33 kg. cal. for reactions (3) for Cl, Br, and I, respectively.[2] These values give 34.5, 40.3, and 50.7 for the activation energies of the over-all reactions, respectively, which compare very well with the figures in Table II. A more complete analysis would have to take into account the rates of the back reactions, but this is usually a minor factor.

TABLE II.—CALCULATED ACTIVATION ENERGIES FOR REACTIONS OF HALOGENS WITH HYDROGEN IN KILOCALORIES[1]

		F	Cl	Br	I
I.	$H_2 + X_2 \rightarrow 2HX$	79	75	62	40*
II.	$\frac{1}{2}X_2 \rightarrow X\ (\Delta H_0)$	31.3	28.5	22.6	17.7
	$X + H_2 \rightarrow HX + H$	0(exo)	0.9	16.4	32.2
	Sum = A (over all)	31.3	29.4	39.0	49.9

* Experimental value from Bodenstein, reference given below.

These activation energies apply only to the noncatalytic, thermal actions. The reactions with Cl and Br (and probably with F, too) roceed more rapidly under the influence of light or if catalyzed by H, a, or K atoms.

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[1] EYRING, *J. Am. Chem. Soc.*, **53**, 2537 (1931).

[2] MORRIS and PEASE, *J. Chem. Phys.*, **3**, 796 (1935).

The noncatalytic homogeneous combination of H_2 and F_2 would not e expected to proceed at room temperature or below, since an activation nergy of 31.3 kg. cal. corresponds to a measurable reaction rate only bove about 100°C. Eyring and Kassel experimentally confirmed the onreactivity of mixtures of H_2 and F_2 at ordinary temperatures and howed that the explosive reactions sometimes observed were probably ue to surface catalysis.[1]

The reaction between H_2 and I_2 is one of the best known bimolecular eactions and was studied extensively by Bodenstein in the temperature ange of 200 to 500°C.[2]

Substitution Halogenation.—One might expect mechanisms analogous o those for the reactions with hydrogen. Three possible mechanisms, sing methane as an example, would be

$$\text{I.}\quad CH_4 + X_2 \rightarrow CH_3X + HX \qquad (5)$$

$$\text{II.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (6) \\ X + CH_4 \rightarrow CH_3X + H & (7) \\ H + X_2 \rightarrow HX + X & (8) \\ \text{etc., etc.} \end{cases}$$

$$\text{III.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (9) \\ X + CH_4 \rightarrow HX + CH_3 & (10) \\ CH_3 + X_2 \rightarrow CH_3X + X & (11) \\ \text{etc., etc.} \end{cases}$$

The activation energies for the bimolecular mechanism have never been calculated; but in the case of chlorine and bromine, at least, it is known that the reaction is a chain reaction because of the inhibitory effect of oxygen. Table III gives the activation energies for the two possible chain mechanisms calculated by the bond energy method. Reactions of types (8) and (11) are always exothermic and therefore fast.

TABLE III.—CALCULATED ACTIVATION ENERGIES FOR REACTIONS OF HALOGENS WITH METHANE IN KILOCALORIES

		F	Cl	Br	I
II	$\tfrac{1}{2}X_2 \rightarrow X$ (ΔH_0)	31.3	28.5	22.6	17.7
	$X + CH_4 \rightarrow CH_3X + H$	0(exo)	21.1	34.7	49.0
	Sum = A (over-all)	31.3	49.6	57.3	66.7
III	$\tfrac{1}{2}X_2 \rightarrow X$ (ΔH_0)	31.3	28.5	22.6	17.7
	$X + CH_4 \rightarrow CH_3 + HX$	0(exo)	0(exo)	0.3	16.1
	Sum = A (over-all)	31.3	28.5	22.9	33.8

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[1] EYRING and KASSEL, *J. Am. Chem. Soc.*, **55**, 2796 (1933).

[2] BODENSTEIN, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1898).

These figures indicate that the reactions with Cl and Br probably follow mechanism III; the reaction with F may follow either mechanism II or III (but probably not mechanism I by analogy with the hydrogen reactions); and the reaction with I may follow either mechanism I or III. Pease and Walz found the experimental activation energy of the chlorination of methane to be 31.6 kg. cal., which compares well with 28.5 kg. cal. given in Table III.[1] The chain mechanism for Cl is confirmed by the strong inhibitory effect of oxygen.

The chlorination of paraffins is promoted by light and catalyzed by H, Na, and K atoms just as is the reaction with hydrogen. In addition, it is catalyzed by lead tetra-alkyls or other source of free alkyl radicals that initiate chains.

The substitution halogenation of olefins (*i.e.*, substitution of hydrogens on olefinic carbons only) would be expected to proceed by the same mechanisms as the halogenation of paraffins; and from the simple bond energy point of view, the activation energies would be expected to be about the same in the two cases. However, Sherman, Quimby, and Sutherland have calculated the activation energies for the substitution halogenation of ethylene by quantum mechanics with the following results given in kilocalories:[2]

	Cl	Br	I
Bimolecular reaction	43.4	46.0	51.2
Chain reaction	45.0	47.0	54.0

Unfortunately these differences are not sufficiently large to say which is probably the true mechanism, in view of the uncertainties in the method of calculation. However, it is interesting to note that regardless of the mechanism, they are all much higher than the corresponding activation energies for the halogenation of methane, indicating that the substitution halogenation of ethylene should be much slower than that of methane and other paraffins. This is indeed the case, as will be discussed below.

Addition Halogenation.—Two possible mechanisms for this type of reaction, using ethylene as an example, would be

$$\text{I.}\quad C_2H_4 + X_2 \rightarrow CH_2X{\cdot}CH_2X \qquad (12)$$

$$\text{II.}\quad \begin{cases} \tfrac{1}{2}X_2 \rightarrow X & (13) \\ X + C_2H_4 \rightarrow CH_2{\cdot}CH_2X & (14) \\ CH_2{\cdot}CH_2X + X_2 \rightarrow CH_2X{\cdot}CH_2X + X & (15) \\ \text{etc., etc.} & \end{cases}$$

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[1] PEASE and WALZ, *J. Am. Chem. Soc.*, **53**, 3728 (1931).

[2] SHERMAN, QUIMBY, and SUTHERLAND, *J. Chem. Phys.*, **4**, 732 (1936).

Mechanism I is a simple bimolecular mechanism, whereas mechanism II is a chain reaction. Still a third over-all reaction is possible, $C_2H_4 + X_2 \rightarrow CH_3{\cdot}CHX_2$, but this involves a molecular rearrangement, and no reasonable mechanism can be deduced for it. Calculation of the activation energies of mechanisms I and II have been made by Sherman, Quimby, and Sutherland with the following results (in kilocalories):

	Cl	Br	I
Bimolecular reaction	25.2	24.4	22.4
Chain reaction	28.5	22.6	20.5

Again, these values are too close together to draw any conclusions, in view of the possible errors in the calculations. The fact that oxygen has a strong inhibitory effect on the chlorination of ethylene indicates that it is probably a chain reaction. However, the activation energy for either mechanism is much lower than that for the corresponding substitution halogenation of ethylene, so that addition on ethylene would be expected to be much faster than substitution. This is born out by experimental results, as will be discussed below.

Hydrochlorination-dehydrochlorination.—Activation energies have never been measured or calculated for the simplest reactions of this type involving ethylene and ethyl chloride. However, Sherman, Quimby, and Sutherland have calculated activation energies for the following reactions:

$$CH_2X{\cdot}CH_2X \rightarrow C_2H_3X + HX \tag{16}$$
$$C_2H_3X + HX \rightarrow CH_2X{\cdot}CH_2X \tag{17}$$

which lead to some interesting conclusions.

Considering first reaction (16), they calculated activation energies as follows (in kilocalories):

	Cl	Br	I
Unimolecular reaction	75.7	68.3	64.2
Chain reaction, catalyzed by X_2	57.0	46.0	51.2

These values probably have little meaning in absolute magnitude; but in a relative sense they show that the X_2-catalyzed chain reaction should be much faster than the unimolecular thermal decomposition. This prediction is confirmed by the observed catalytic effect of chlorine in promoting dehydrochlorination. Mugdan and Barton reported dehydrochlorination of ethylene dichloride to vinyl chloride and HCl in the presence of ½ per cent chlorine as 30 per cent at 300°C., 50 per cent at 350°C., and 70 per cent at 370°C. for a flow rate of 38 gr. per hr. through a 600-mm. length of hot zone.[1] In the absence of chlorine, there was only 2 per cent dehydrochlorination at 400°C. and 30 per cent at 500°C. with the same experimental setup. The mechanism used by Sherman, Quimby, and Sutherland for this catalyzed chain reaction was as follows:

$$\tfrac{1}{2}X_2 \rightarrow X \tag{18}$$

$$X + CH_2X{\cdot}CH_2X \rightarrow CHX{\cdot}CH_2X + HX \tag{19}$$

$$CHX{\cdot}CH_2X \rightarrow C_2H_3X + X \tag{20}$$

etc., etc.

Considering now reaction (17), Sherman, Quimby, and Sutherland calculated activation energies as follows:

	Cl	Br	I
Bimolecular reaction	43.5	41.9	36.4
Chain reaction	39.3	29.0	27.7

The activation energies of the chain reactions are clearly lower, and their relative values are in agreement with the experimental fact that HBr and HI add to ethylene readily whereas HCl does so much more slowly, except in the presence of a catalyst such as $FeCl_3$.

CHLORINATION OF HYDROCARBONS AND CHLOROHYDROCARBONS

The published knowledge under this heading is well summarized in three papers and several patents by Vaughan and Rust[2,3,4,5]. Certain data extracted from these papers and patents are summarized in Tables IV*A* and IV*B*. These data are rather fragmentary and represent comparable rate data only in a rough way. Nevertheless, intercomparison of these figures leads to some interesting conclusions.

1. *The rate of substitution chlorination of hydrogens on saturated carbons is greater than the rate of substitution of hydrogens on unsaturated carbons.* This conclusion is evident from a comparison of ethane and propane with ethylene and vinyl chloride. In fact, the rate of substitution on paraffins is greater than the rate of substitution plus addition on unsaturates. The difference in rate is such that, in the chlorination of mixtures of paraffins and olefins, substitution on paraffins (or on saturated carbons

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[1] U. S. 2,378,859 (1945).

[2] VAUGHAN and RUST, *J. Org. Chem.*, **5**, 449 (1940).

[3] RUST and VAUGHAN, *J. Org. Chem.*, **5**, 472 (1940).

[4] RUST and VAUGHAN, *J. Org. Chem.*, **6**, 479 (1941).

[5] U. S. 2,246,082 (1941); 2,249,922 (1941); 2,278,527 (1942); 2,284,479 (1942); 2,284,482 (1942); 2,299,441 (1942).

TABLE IV*A*.—DATA ON CHLORINATION OF HYDROCARBONS AND CHLOROHYDROCARBONS[1]

	240°C.	280°C.	320°C.	360°C.	400°C.
Ethane	19	85	95		
Propane	18	97			
To 1-chloropropane	9				
To 2-chloropropane	9				
Ethylene	11	60	. .	Large	Large
Substitution	1	8	. .	Large	Large
Addition	10	52	. .	Small	Small
Propylene	26	80	. .	Large	Large
Substitution	10	50	. .	Large	Large
Addition	16	30	. .	Small	Small
Ethyl chloride	7	26	59	96	100
To 1, 1-dichloroethane	. .	. .	47		
To 1, 2-dichloroethane	. .	. .	12		
Vinyl chloride	12	47	72	84	90
Substitution	0	1	19	54	84
Addition	12	46	53	30	6

[1] Figures are percentage of Cl_2 reacted for mixture 1 mole Cl_2: 2 moles reactant: 3 moles N_2 or CO_2 at total flow rate of 300 cc. per min.

TABLE IV*B*.—DATA ON CHLORINATION OF PROPYL AND BUTYL CHLORIDES[1]

	200–208°C.	260°C.	312–319°C.	340°C.	380–383°C.
n-Propyl chloride:					
To 1, 1-dichloropropane	. .	14	. .	6	34
To 1, 2-dichloropropane	. .	24	. .	4	0
To 1, 3-dichloropropane	. .	14	. .	7	36
Isopropyl chloride:					
To 1, 2-dichloropropane	40	. .	22	. .	21
To 2, 2-dichloropropane	50	. .	32	. .	64
n-Butyl chloride:					
To 1, 1-dichlorobutane	15	. .	17	. .	10
To 1, 2-dichlorobutane	14	. .	0	. .	0
To 1, 3-dichlorobutane	59	. .	43	. .	23
To 1, 4-dichlorobutane	40	. .	38	. .	17
sec-Butyl chloride					
To 1, 2-dichlorobutane	0	. .	0	. .	0
To 1, 3-dichlorobytane	31	. .	33	. .	32
To 2, 2-dichlorobutane	19	. .	22	. .	22
To 2, 3-dichlorobutane	30	. .	16	. .	0

[1] Figures are grams of product recovered in particular experiments.

in olefins) is the predominant reaction, particularly above 300°C. This is illustrated by the chlorination of a mixture of 1 mole Cl_2:1 mole C_2H_6:1 mole C_2H_4:3 moles N_2 at 314°C. at a total flow rate of 300 cc. per min., which gave a product 67.8 mole per cent ethyl chloride, 22.6 per cent

1, 1-dichloroethane, 3.6 per cent vinyl chloride, 2.5 per cent 1, 2-dichloroethane, 2.2 per cent 1, 1, 1-trichloroethane, 1.3 per cent heavier products. Another illustration is the technically important chlorination of propylene at temperatures of 350°C. and up, which gives a high yield of allyl chloride. Quantitatively, it may be noted that the total rate of substitution of the paraffinic portion of propylene (3 hydrogens) is about one-half the rate of substitution of ethane (6 hydrogens).

Conclusion 1 was predicted by the calculated activation energies of Sherman, Quimby, and Sutherland despite the large errors possible in the quantum mechanical methods used. They calculated activation energies of about 30 and 45 kg. cal., respectively, for the substitution chlorination of paraffinic and olefinic hydrogens.

2. *The rate of substitution chlorination of hydrogens on saturated carbons is greater than the rate of addition chlorination to double bonds at high temperatures; the reverse is true at low temperatures.* See the discussion under conclusion 1. The calculated activation energies for the two reactions are 28.5 and 25.2 kg. cal., respectively, but these calculated values are too close together to draw valid conclusions.

3. *The rate of addition chlorination on double bonds is greater than the rate of substitution of hydrogens on unsaturated carbons.* This is certainly true at temperatures around 240 to 280°C., as shown by the data for ethylene and vinyl chloride in Table IVA. It may also be true at higher temperatures, despite the data in Table IVA, since the substituted products that predominate at higher temperatures may be formed by addition of chlorine followed by a rapid dehydrochlorination to reach or approach equilibrium. The relative amounts of substitution and addition products as a function of temperature given in Table IVA are approximately the equilibrium amounts for this reaction.

The theoretically calculated activation energies, 25.2 kg. cal. for addition chlorination and 43.4 kg. cal. for substitution of ethylenic hydrogens, are in agreement with conclusion 3.

4. *The rate of substitution of hydrogens α to a chlorine is about the same as the normal rate of substitution of hydrogens on the type of carbon atom concerned.* The rate of substitution of ethyl chloride (largely on the 1-carbon atom) at 260 and 280° is about one-third the rate of substitution of ethane, which has six equivalent hydrogen atoms.

5. *The rate ot substitution of hydrogens β to a chlorine is markedly less than the normal rate of substitution of hydrogens on the type of carbon atom concerned.* Compare the results of chlorination of propyl and butyl chlorides, giving proper weight to the relative rates of substitution of hydrogens on primary and secondary carbon atoms. This effect is more pronounced with increasing temperature so that the amounts of 1, 2-dichloropropane, 1, 2-dichlorobutane, and 2, 3-dichlorobutane

decrease relative to the 1, 1; 2, 2; and 1, 3 types of compounds with increasing temperature.

6. *The rate of substitution of hydrogens γ to a chlorine is only slightly less than the normal rate of substitution of hydrogens on the type of carbon atom concerned. For hydrogens δ and farther removed from a chlorine, the rate of substitution is the normal one.* Compare the amounts of 1, 3-dichloropropane, 1, 3-dichlorobutane, and 1, 4-dichlorobutane obtained, giving proper weight to the relative rates of substitution of hydrogens on primary and secondary carbon atoms.

A number of other interesting semiquantitative deductions can be drawn from the above data, which will be left to the reader. There do not appear to be any theoretical considerations bearing on conclusions 4, 5, and 6.

The substitution chlorination of hydrocarbons in the presence of oxygen to give greater yields of chlorinated product for a given consumption of Cl_2 reported by Cass is an equilibrium effect in the oxidation of HCl to Cl_2 according to the Deacon reaction.[1] Equilibrium is in favor of Cl_2 in the Deacon reaction at all temperatures below about 600°C.[2] This reaction must be carried out at a sufficiently high temperature to overcome the inhibitory effect of oxygen on the substitution reaction but yet low enough to have favorable equilibrium in the Deacon oxidation reaction.

III. SURVEY OF HALOGENATIONS

CHLORINATION

Chlorination of Paraffins.—It is difficult to overestimate the economic importance of the compounds obtained by the halogenation of the saturated and unsaturated lower paraffins.[3] To a considerable extent, these halogeno derivatives are used per se as cleaning fluids ($CHCl{=}CCl_2$); refrigerants (CCl_2F_2); plant stimulants ($CH_2Cl{\cdot}CH_2Cl$); anesthetics ($CHCl_3$); general solvents (CCl_4); etc. By and large, however, the saturated and unsaturated halogeno paraffins are used as the raw materials for an exceedingly large number of syntheses, *e.g.*, the preparation of alcohols, alkylene oxides, ethers, amines, hydrocarbons, alkaryl compounds, etc. Because the paraffinic hydrocarbons and chlorine are widely available and cheap, this segment of chemical activity has increased greatly in recent years and is destined further to expand.

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[1] U. S. 2,327,174 (1943).

[2] LEWIS and RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

[3] In 1944, the combined output of chlorinated paraffins in the United States was about 800 million pounds, or equal to the total production of all the important aromatic intermediates including styrene for the rubber program and phthalic anhydride for resin manufacture.

1. Halogenation with Chlorine Gas

Chlorination Rules, Paraffins.—On the basis of extensive research, Hass and coworkers have postulated the following rules regarding the chlorination of paraffins.[1] Such operations can be carried out in the apparatus shown diagrammatically in Figs. 11 and 13.

CHLORINATION RULES

1. Carbon skeleton rearrangements do not occur during either photochemical or thermal chlorinations if pyrolysis temperatures are avoided; every possible monochloride derivative without such rearrangement is always formed. As far as is known, this generalization extends also to the polychlorides. The boiling-point data for the lower paraffin monochlorides are given in Table V.

TABLE V.—BOILING-POINT DATA, CHLOROALKANES[1]

Compound	B.p. or range, °C.	B.p. of corresponding alcohol, °C.
2-Chloropropane	34.8	82.26
1-Chloropropane	46.60	97.18
2-Chloroisobutane	51.0	82.86
2-Chlorobutane	68.25	99.53
1-Chloroisobutane	68.85	107.89
1-Chlorobutane	78.50	117.71
1-Chloro-2, 2-dimethylpropane	84.4	114.0
2-Chloro-2-methylbutane	85.7	101.8
2-Chloro-3-methylbutane	92.9–93.0*	110.0–111.5
3-Chloropentane	97.1–97.4	115.40
2-Chloropentane	96.6–96.8	119.28
1-Chloro-2-methylbutane	99.9	128.0
1-Chloro-3-methylbutane	98.8	132.00
1-Chloropentane	108.35	138.00

[1] Corrected to 760 mm.; value in literature is 91.8 to 91.9°C. at 736 mm.

2. The hydrogen atoms are always substituted at rates that are in the order primary < secondary < tertiary. At 300°C. with reaction in vapor phase, these relative rates are 1.00:3.25:4.43. The data in Table VI present the evidence for this rule, the experimental results serving as a basis for the calculation of the empirical constants noted above. The

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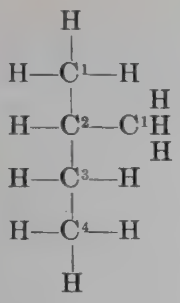
[1] HASS and MARSHALL, *Ind. Eng. Chem.*, **23**, 352 (1931); HASS, MCBEE, and WEBER, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936); HASS and WEBER, *Ind. Eng. Chem., Anal. Ed.*, **7**, 231 (1935); HASS, MCBEE, and HATCH, *Ind. Eng. Chem.*, **29**, 1335 (1937).

method of computation will readily be illustrated by using a specific example, in this case isopentane:



$$6 \times 1.00 = 6.00; \qquad \frac{6.00 \times 100}{19.93} = 30.1\%$$

1-Chloro-2-methylbutane

$$1 \times 4.43 = 4.43; \qquad \frac{4.43 \times 100}{19.93} = 22.2\%$$

2-Chloro-2-methylbutane

$$2 \times 3.25 = 6.50; \qquad \frac{6.50 \times 100}{19.93} = 32.6\%$$

3-Chloro-2-methylbutane

$$3 \times 1.00 = \frac{3.00}{19.93}; \qquad \frac{3.00 \times 100}{19.93} = 15.1\%$$

4-Chloro-2-methylbutane

There are six hydrogen atoms attached to carbon atoms in the positions numbered 1 in the formula. These are primary hydrogen atoms, and their relative reaction rate is arbitrarily taken as 1.00. The product of the number of hydrogen atoms in this position multiplied by the relative reaction rate gives the chance of the chlorine substituting in this position to yield 1-chloro-2-methylbutane. The sum of all such products for isopentane under these conditions is 19.93, so 6 × 100/19.93 gives the percentage of 1-chloro-2-methylbutane in the monochlorides. A reversal of this calculation enables us to obtain the relative reaction rates from the composition of the monochloride mixtures. It is understood in applying the rule that conditions must be selected so that pyrolysis is substantially eliminated and only a very small amount of monochloride is carried to a higher state of chlorination.

TABLE VI.—CHLORINATION OF PARAFFINS, OBSERVED AND CALCULATED ISOMERIC RATIOS AT 300°C.

Hydrocarbon	Isomeric Monochloride, %							
	-1-Chloro		-2-Chloro		-3-Chloro		-4-Chloro	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Propane	48	48	52	52				
2-Methylpropane	67	67	33	33				
Butane	32	32	68	68				
2-Methylbutane	33.5	30	22	22	28	33	16.5	15
n-Pentane	23.8	23.5	48.8	51	27.4	25.5		

3. At increasing temperatures, there is increasingly close approach to relative rates of 1 : 1 : 1 in both liquid and vapor phase.

Evidence for this generalization is given in Fig. 1, where the relative rates of secondary and tertiary hydrogen atoms are shown to vary with temperature in both vapor and liquid phases. The relative substitution rate of a primary hydrogen atom is taken as 1.

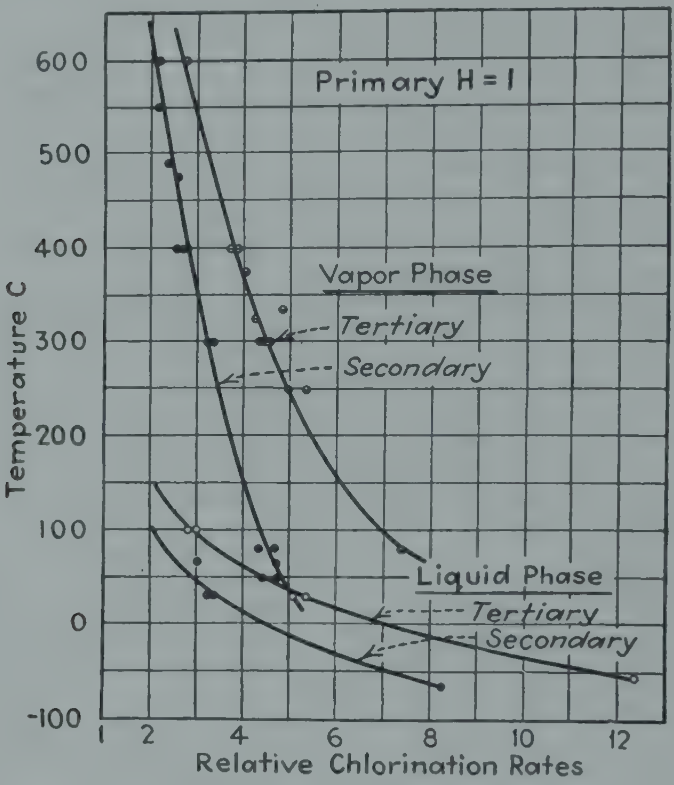


FIG. 1.—Rule 3, halogenation.

By the use of these graphs, one can find the relative reaction rates that may be used as shown previously to obtain the isomeric ratios. With this information available, it is easy to estimate from the structural formula of any paraffin hydrocarbon the relative proportions of the various isomeric monochlorides that can be obtained by chlorination under any of the conditions covered by the graph.

Certain precautions must be observed in applying these curves. The different monochlorides may chlorinate to dichlorides, trichlorides, etc., at different rates. This would change their ratios in the monochloride fraction so that results are most accurate when not more than a small proportion of monochloride is converted to dichloride. This is the condition always used in commercial operations for obtaining monochlorides, for reasons of economy. At low temperatures, where substantially no olefin formation occurs, results are not complicated by selective pyrolysis; but when operating at temperatures above 300°C., one can easily get the impression that a nonselective chlorination is taking place, whereas actually the tertiary and/or secondary chlorides are being preferentially decomposed. When pyrolysis becomes appreciable, (*a*) the organic chlorine fails to balance the chlorine present as hydrochloric acid; (*b*) olefins appear in the recovered hydrocarbon; and (*c*), especially if recycling is used, chloroolefins appear in the organic chloride fractions.

4. Liquid-phase chlorination gives relative rates of primary, secondary, and tertiary substitution which are obtainable only at much higher temperature in vapor phase. This is obvious from an inspection of Fig. 1.

A given temperature change produces a much greater difference in relative reaction rates of primary, secondary, and tertiary hydrogens when one is operating in liquid phase than when the chlorination takes place in gaseous phase. This means that the isomeric ratios are much more readily controllable in liquid than in vapor phase. Maximum yields of either primary isomers (at high temperatures) or secondary or tertiary isomers (at low temperatures) can be obtained by operating with the reagents in liquid form. In case the critical temperature of the hydrocarbon is inconveniently low, the chlorination may be carried out using carbon tetrachloride as a solvent.

5. The presence or absence of the following factors does not affect appreciably the relative rates of primary, secondary, and tertiary substitution; (*a*) moisture; (*b*) carbon surfaces; and (*c*) light.

6. Excessive temperatures and/or reaction times result in appreciable pyrolysis of the chlorides in the order primary < secondary < tertiary.

This has already been commented on in connection with rule 3 insofar as excessive temperatures are concerned, but it may be added that the extent of the pyrolysis is more than would be predicted from data obtained by passing the pure chlorides through a hot reactor in the absence of chlorine. This result would be expected on the basis of free radical formation, since the radicals may decompose as follows:

$$C_nH_{2n+1} \rightarrow C_nH_{2n} + H$$

The free hydrogen atoms would continue the chlorination chain as follows:

$$H + Cl_2 \rightarrow HCl + Cl$$

Excessive polychloride formation is presumably caused by the following type reactions:

$$\begin{aligned} C_5H_{11}Cl &\rightarrow C_5H_{10} + HCl \\ C_5H_{10} + Cl_2 &\rightarrow C_5H_{10}Cl_2, \text{ etc.} \end{aligned}$$

7. If a molar excess of hydrocarbon is used and the chlorination conditions are maintained constant, the yield of monochlorides *vs.* polychlorides may be obtained from the equation

$$X = KY$$

where X = weight ratio of monochlorides over polychlorides.
Y = ratio of moles of hydrocarbon over moles of chlorine.
K = a constant peculiar to the hydrocarbon and the conditions.

As evidence, Fig. 2 is presented. In applying this graph, conditions are chosen so that all the chlorine reacts.

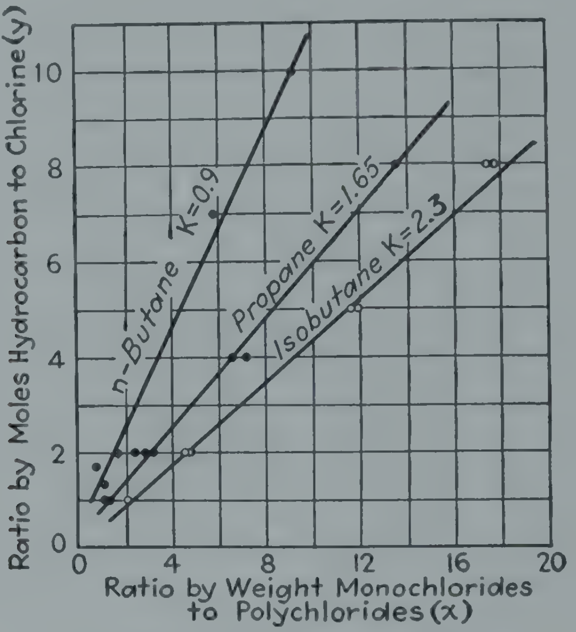


FIG. 2.—Rule 7, halogenation.

The practical import of rule 7 is that the yield of overchlorinated material may be suppressed to any desired degree if only a small percentage of the material to be chlorinated is allowed to react at each pass through the chlorinator. This applies to any stage of chlorination. An economic balance must be struck between the advantages of the higher yields of monochlorides, which are caused by the lower chlorine concentrations in the reacting hydrocarbon, and the increased cost of additional recycling. When chlorination is achieved thermally, recycling involves the expense of heating and cooling large quantities of materials. In the case of the further thermal chlorination of the homologous alkyl chlorides, too many passes through the hot reactor may increase the amount of pyrolysis unduly, so that too much recycling is undesirable from that standpoint also.

One of the advantages of liquid-phase thermal chlorination is that because of the lower temperatures involved, the pyrolysis is almost completely eliminated and the amount of heat put into the reacting materials and removed from the reaction products is lessened.

8. Dichlorination proceeds by two mechanisms: (*a*) loss of hydrogen chloride followed by addition of chlorine to the resulting olefin and (*b*) progressive substitution. Slow, thermal chlorination favors mechanism

1, whereas with rapid, liquid-phase or vapor-phase, single-pass thermal reaction or low-temperature photochemical conditions, mechanism 1 is substantially eliminated.

In view of the large amount of work that has been performed on the addition of chlorine to olefin bonds, it is evident that conditions conducive to the formation of unsaturates must result in at least some union of chlorine with these products, unless the temperature is too high. Thus, a prolonged vapor-phase thermal chlorination of *n*-pentane at 100°C. in the absence of light yields a much higher ratio of polychlorides to monochlorides than if the reaction is carried out rapidly at the same temperature in the presence of light. This is due to the pyrolysis of the secondary chlorides which, though very slow, is appreciable at this temperature, followed by saturation of the double bonds with chlorine.

Conclusive evidence that dichlorination occurs also by progressive substitution is available in the formation of large quantities of 1, 3-disubstitution products which cannot be produced by the addition, under these conditions, of either hydrogen chloride or chlorine to any olefin or chloroolefin.

9. In vapor-phase chlorination, the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution.

The data obtained in the dichlorination of propane and isobutane shows that only small amounts of dichlorides containing both chlorine atoms on the same carbon atom are found to be present. In the case of propane, the boiling points of the dichlorides are as follows: 2, 2-dichloride, 69.7°C.; 1, 1-dichloride, 86°C.; 1, 2-dichloride, 96.8°C.; 1, 3-dichloride, 120.4°C. A rectification analysis (Fig. 5, page 194) is therefore conclusive and relatively easy.

10. In vapor-phase chlorination of saturated hydrocarbons, increased pressure causes increased relative rates of primary substitution. The influence of pressure, in the chlorination of propane in the vapor phase, is shown by the curve of Fig. 3.

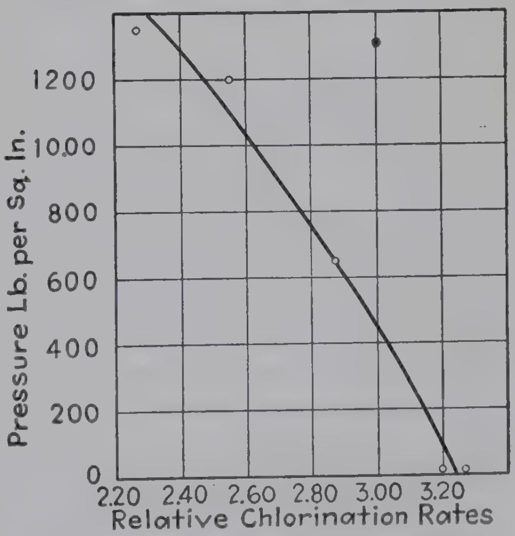


FIG. 3.—Chlorination of propane, at 300°C. Effect of pressure upon relative chlorination rates of primary and secondary hydrogen atoms.

Substitution Reactions.—The reaction of chlorine gas with vapors of paraffin hydrocarbons is so vigorous that precautions must be taken to avoid the sudden development of excessive temperatures and pressures. Consequently, numerous procedures have been devised to avoid decomposition and diminished yield of the desired product. The following are some of the methods that have been proposed for moderating and controlling the reaction:

1. Employing a considerable excess of the hydrocarbon vapors.
2. Carrying out the reaction in the presence of diluent gases such as nitrogen, steam, or the hydrogen chloride that is liberated.
3. Introducing the reacting gases into a liquid cosolvent.
4. Employing a halogen gas that reacts mildly and then replacing the combined halogen with chlorine.
5. Effecting chlorination in successive stages by mixing only part of the chlorine with the hydrocarbon.

Treatment of Gaseous Aliphatic Compounds. *Chlorination of Methane.*—The chlorination of methane can most economically be accomplished by treating a mixture of chlorine with an excess of the hydrocarbon at elevated temperatures. Actinic rays, iodine, and the chlorides of copper, iron, and antimony have been suggested as catalysts for this reaction.

In the thermal method, a close correlation between temperature and reaction time must be observed. Temperatures of approximately 300° may be used at relatively long contact periods, whereas 0.01 sec. is sufficient for operations at 800 to 850°. The products of chlorination depend on the temperature and the chlorine ratio; but in all cases a mixture is obtained. It is possible, however, to control conditions to obtain a preponderance of one of the chloromethanes.

When methane and chlorine in a ratio of 9:1 are conducted over a partially reduced cupric chloride catalyst containing 1 per cent cerium chloride at 450°, an 89 per cent yield of methyl chloride is obtained.[1] Carbon tetrachloride is the principal product when methane, chlorine, and hydrogen chloride in a ratio of 16:64:80 to 100 are passed over activated carbon at 525 to 530°.[2]

When steam is employed as a diluent, extensive hydrolysis of the chlorohydrocarbons occurs.

Chlorination of Ethane.—Ethyl chloride is readily and economically obtained either by the esterification of ethanol with hydrochloric acid in the presence of zinc chloride or by the reaction of ethylene and hydrogen chloride in the presence of aluminum chloride. The di- and polychlorides of ethane can be prepared by direct addition of chlorine to ethylene in a liquid bath of dichloroethane, the more chlorinated derivatives being obtained at temperatures sufficiently high to permit substitution.

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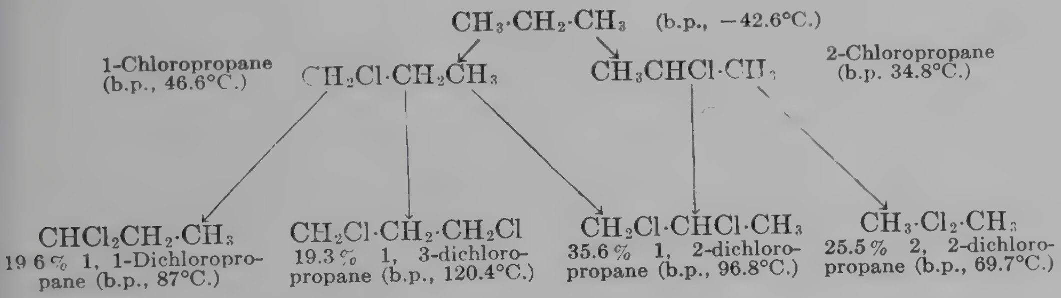
[1] GIORDANI, *Ann. chim. appl.*, **25**, 163 (1935).

[2] KIPRIANOV and KUSNER, *J. Appl. Chem.*, **8**, 673 (1935).

The thermal chlorination of ethane is carried out in the presence of contact agents such as iron, charcoal, and pumice impregnated with cupric chloride, at 300 to 350°. Ratios of 8 to 10:1 ethane to chlorine are used; but in all cases the product contains polychlorinated derivatives. In the presence of light from a mercury vapor lamp, the chlorination of ethane results in the formation of mono- to hexachloroethanes as well as some ethylidene chloride. When carbon tetrachloride is used as a solvent, it is feasible to effect the chlorination in the liquid phase.

Chlorination of Propane.—When propane is chlorinated under conditions that avoid excessive pyrolysis, every possible monochloride and polychloride derivable without carbon-skeleton rearrangement is always formed in accordance with Hass's rule.[1] According to this generalization, the chlorination of propane to the dichloride stage occurs according to the following diagram.[2]


CH₃·CH₂·CH₃ (b.p., −42.6°C.)
1-Chloropropane (b.p., 46.6°C.)
CH₂Cl·CH₂CH₃
CH₃CHCl·CH₃
2-Chloropropane (b.p. 34.8°C.)
CHCl₂CH₂·CH₃
19.6% 1, 1-Dichloropropane (b.p., 87°C.)
CH₂Cl·CH₂·CH₂Cl
19.3% 1, 3-dichloropropane (b.p., 120.4°C.)
CH₂Cl·CHCl·CH₃
35.6% 1, 2-dichloropropane (b.p., 96.8°C.)
CH₃·Cl₂·CH₃
25.5% 2, 2-dichloropropane (b.p., 69.7°C.)

The dichlorination may be carried out in apparatus shown diagrammatically in Fig. 4, at 150 to 250° and preferably under superatmospheric pressures.[3]

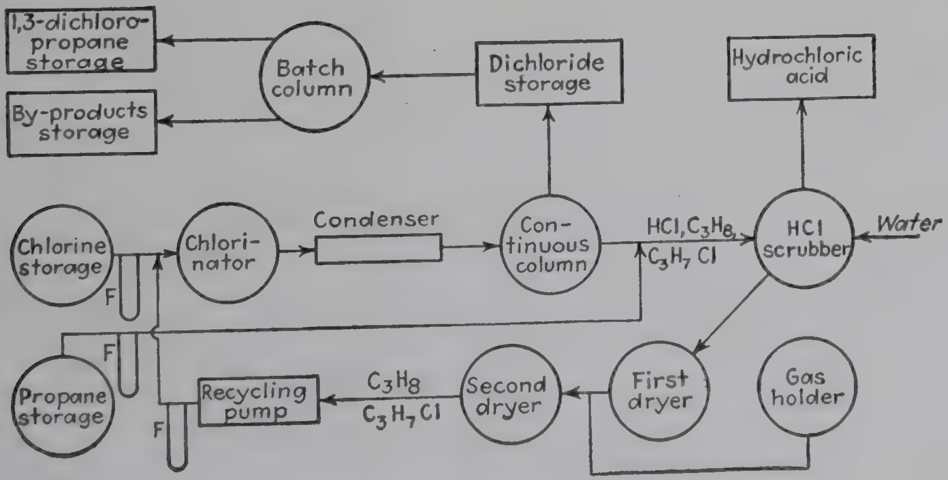

1,3-dichloropropane storage
By-products storage
Batch column
Dichloride storage
Hydrochloric acid
Chlorine storage
Chlorinator
Condenser
Continuous column
HCl, C₃H₈
C₃H₇Cl
HCl scrubber
Water
F
F
F
Propane storage
Recycling pump
C₃H₈
C₃H₇Cl
Second dryer
First dryer
Gas holder

Fig. 4.—Flow diagram, chlorination of propane.

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[1] Hass, McBee, and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935).

[2] Hass, McBee, and Hatch, *Ind. Eng. Chem.*, **28**, 1178 (1936).

[3] Hass and McBee, U. S. 2,105,733 (1938).

By means of flowmeters *F*, a molar excess of material to be chlorinated (propane and monochlorides) over chlorine, of approximately 10:1, is maintained in the gases flowing to the chlorinator. This excess, in combination with complete removal of dichlorides from the recycled gas by means of the continuous rectifying column, ensures a low concentration of trichlorides in the crude dichloride mixture. The chlorine is allowed to react completely in the chlorinator, and the material flowing to the condenser and hence to the continuous rectifying column consists essentially of propane, both monochloropropanes, all four dichloropropanes, and hydrogen chloride. The effluent from the base of the continuous column consists of dichloropropanes with minor amounts of more highly chlorinated material. The hydrogen chloride, propane, and monochlorides pass up through the column in which a sufficient monochloride reflux is maintained to remove the dichlorides efficiently from the overhead product. The make-up propane is introduced immediately after the continuous column and assists in preventing condensation of monochlorides in the hydrochloric acid scrubber, in which the hydrogen chloride is removed. The moist gases from the hydrochloric acid scrubber must be dried in order to prevent corrosion in other parts of the plant. This is accomplished in two sulfuric acid scrubbing towers which also remove olefins and chloroolefins which are formed in traces in the chlorinator. The gas holder serves as a guide to the rate of flow in the make-up propane, which is adjusted to keep the gas holder about half full.

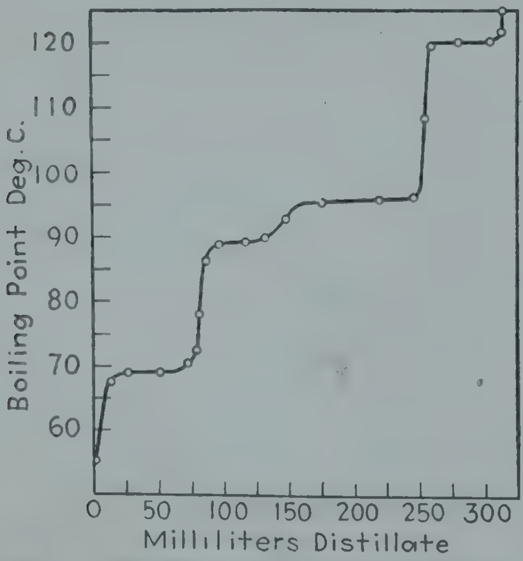


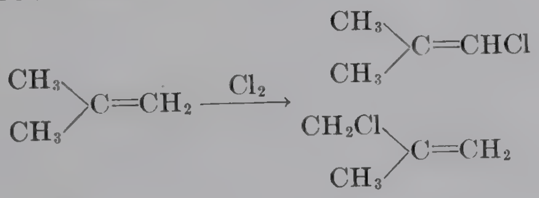
FIG. 5.—Rectification curve for dichloropropanes.

The crude dichlorides are fractionated in the batch rectifying column. When 1, 3-dichloropropane is wanted for the preparation of the anesthetic cyclopropane, it is separated from all other chlorinated products except 1, 2, 2-trichloropropane. This trichloride (b.p., 123°C.) boils only 1.6°C. higher than the 1, 3-dichloride, and its removal by distillation is therefore impractical. Since only about 8 per cent of the crude dichloride mixture consists of trichlorides, and the 1, 2, 2-trichloropropane is the only one of the five isomers present that is difficultly separable, it occurs in only minor amounts in the rectified 1, 3-dichloropropane. The final elimination of this impurity occurs in the ring-closure reaction where it is converted to 2-chloro-1-propene (b.p., 22.68°C.) which is removed in the rectification of the crude cyclopropane.

Chlorobutanes.—Chlorobutanes can be obtained by diverse procedures, such as (1) the liquid-phase or thermal chlorination of butane, (2) addition of chlorine or hydrogen chloride to butenes, (3) esterification of butanols and butylene glycols, (4) chlorination of chlorobutenes and chlorobutadienes, and (5) hydrochlorination of tetramethylene oxide (tetrahydrofurane).

The thermal chlorination of butane is similar to that of propane and can be carried out according to the procedures developed by Hass and coworkers.[1] The product contains 1-chloro- and 2-chlorobutane as well as 1, 2-dichloro- and 1, 3-dichlorobutanes. In the photochemical chlorination, chlorine is introduced into a body of *n*-butane that is cooled to −25°.[2]

Butene-1 and butene-2 add chlorine in the presence of light at low temperatures to yield 1, 2- and 2, 3-dichlorobutanes, respectively. Isobutylene, however, does not yield a saturated chloro derivative on chlorination. The dichloride addition product loses hydrogen chloride to give the following chlorobutenes:



When a gas mixture containing 1.0 part by weight of *n*-butane and 0.53 part chlorine is passed at a uniform rate into a molten mixture of potassium chloride and aluminum chloride, the products are 20 per cent monochlorobutane, 29.2 per cent butylene, and 44 per cent unreacted butane.[3]

Chlorination of Cycloparaffins.—Cyclohexyl chloride can be made by two general methods: (1) direct chlorination of cyclohexane in the presence or absence of light and (2) hydrochlorination of cyclohexanol. In batch operations, the method of direct chlorination ordinarily leads to the formation of a considerable proportion of polychlorocyclohexanes even when half of the stoichiometric quantity of chlorine is used.

According to the procedures developed by Levine and Cass, cyclohexane admixed with about 3 per cent anhydrous stannic chloride is subjected to the action of dry chlorine in the absence of light.[4] The chlorination is slow but smooth when the temperature is maintained at 40°. A yield of 89 per cent monochlorocyclohexane and about 10 per cent dichlorocyclohexanes is obtained when 38 per cent of the chlorine necessary for complete halogenation is used. When the reaction is carried out in the presence of light in a lead-lined vessel, the reaction is more rapid. A yield of 82.5 monochlorocyclohexane is obtained when 53 per cent of the chlorine necessary for complete monochlorination is introduced.

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[1] Hass, McBee, and Weber, *Ind. Eng. Chem.*, **27**, 1191 (1935); U. S. 2,105,733 (1938).

[2] Carter and Johnson, U. S. 2,381,037 (1945).

[3] Kennedy and Russell, U. S. 2,224,155 (1940)

[4] Levine and Cass, U. S. 2,154,049 (1939).

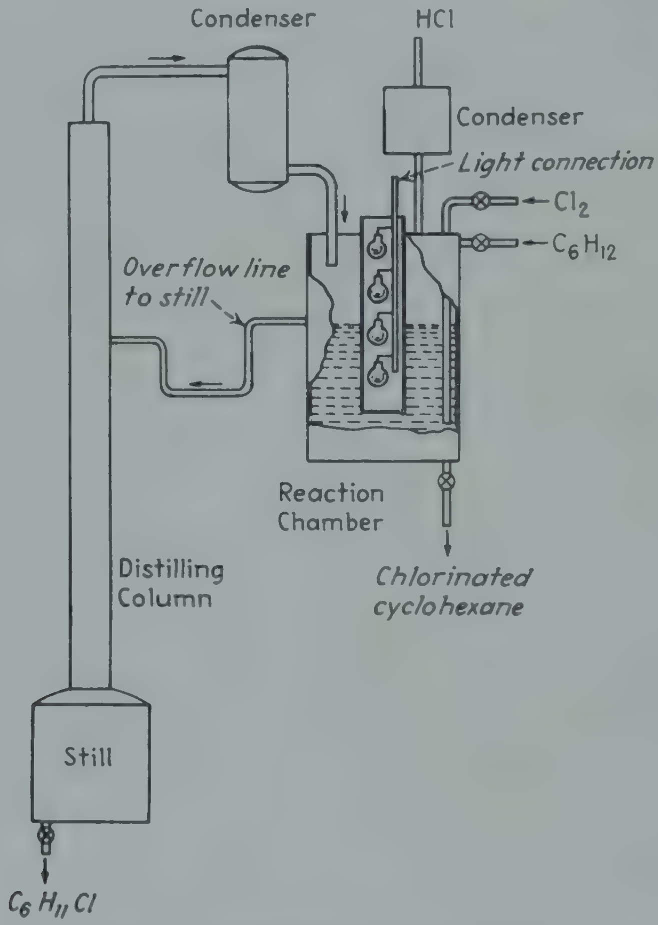
Condenser
HCl
Condenser
Light connection
Cl_2
C_6H_{12}
Overflow line to still
Reaction Chamber
Distilling Column
Chlorinated cyclohexane
Still
$C_6H_{11}Cl$

Fig. 6.—Photochlorination of cyclohexane.

When cyclohexyl chloride is the desired product for use in the preparation of cyclohexylamine or for condensations according to the Friedel and Crafts reaction, it appears advantageous to chlorinate in the presence of light and to use at least a 10:1 molar ratio of cyclohexane to chlorine in a cyclic process.[1] The products of reaction are continuously withdrawn from the reaction chamber to a still (Fig. 6) where the unconverted cyclohexane is distilled off, condensed, and returned to the chlorinator which is provided with an encased battery of electric lights. The chlorinator, which is maintained at 55 to 65°, is preferably made of lead, nickel, or monel metal in order to provide better resistance against the corrosive action of the reaction products. A yield of about 94 per cent cyclohexyl chloride is thus obtained in batch operations when about half of the chlorine theoretically required to convert all the cyclohexane to cyclohexyl chloride has been reacted.

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[1] Britton and Perkins, U. S. 2,287,665 (1942).

Hexachlorocyclohexanes ($C_6H_6Cl_6$), of which the gamma isomer is a useful insecticide, can be made by substitution chlorination of cyclohexane, by the addition chlorination of benzene using light as a catalyst,[1] or by introducing liquid chlorine into benzene in the absence of light.[2] In the Hardie process, chlorine is introduced until about 60 per cent of the benzene has been converted to benzene hexachloride. The solid product is removed by filtration, and chlorination of the benzene-fortified filtrate is continued.

Chlorination of Ethanol.[3] *Chloral.*—When chlorine is bubbled in a regulated manner into 95 per cent ethanol, a series of reactions occur leading to the formation of (chloral) trichloroacetaldehyde.

$$C_2H_5OH + Cl_2 \xrightarrow{\qquad} C_2H_5OCl + HCl \tag{1}$$

$$CH_3CH_2OCl + C_2H_5OH \rightarrow CH_3CH(OH)OC_2H_5 + HCl \tag{2}$$

$$CH_3CH(OH)OC_2H_5 + 3Cl_2 \xrightarrow{80^\circ} CCl_3CH(OH)OC_2H_5 + 3HCl \tag{3}$$

Apparently 4 moles of chlorine are required theoretically for reaction with 2 moles of ethanol. In practice, however, it has been found advantageous to use a ratio of about 2.25 moles of chlorine to 1 mole of alcohol.

The first step in the reaction is the formation of ethyl hypochlorite, which [Eq. (2)] reacts with ethanol to form the hemiacetal and hydrogen chloride. The formation of the acetal $CH_3CH(OC_2H_5)_2$ may also occur, but this will in all probability revert to the monoethyl acetal under the conditions existing in the reaction vessel. The final stage is the chlorination of the hemiacetal to the trichloro derivative [Eq. (3)]. Chloral is obtained by distilling the hemiacetal of trichloroacetaldehyde with sulfuric acid.

Ethyl chloride is obtained as a volatile by-product or coproduct of the reaction, and its formation may be ascribed to the following reactions, although other mechanisms can be written.

$$CH_3CH(OH)OC_2H_5 + Cl_2 \xrightarrow{80^\circ} CH_2ClCH(OH)OC_2H_5 + HCl \tag{4}$$

$$CH_2ClCH(OH)OC_2H_5 + Cl_2 \xrightarrow[H_2O]{85^\circ} CHCl_2CHO{\cdot}H_2O + HCl + (C_2H_5Cl) \tag{5}$$

$$CHCl_2CH(OH)OC_2H_5 + Cl_2 \xrightarrow[H_2O]{85^\circ} CCl_3CHO{\cdot}H_2O + HCl + (C_2H_5Cl) \tag{6}$$

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[1] Hardie, U. S. 2,218,148 (1940).

[2] Bender, U. S. 2,010,841 (1935).

[3] Based on O.P.R.D. research coordinated by W. S. Parks and J. Katz, Rhode Island State College.

The quantity of ethyl chloride formed increases from 28 to 72 per cent of the theoretical as the water content of the alcohol is increased from 0 to 20 per cent (80 per cent ethanol). It is known that ethyl chloride is formed by the decomposition of either the mono-, di-, or trichloroacetaldehyde acetal to the corresponding hydrate by refluxing with the theoretical proportions of concentrated hydrochloric acid. The presence of limited amounts of water in facilitating this reaction presumably accounts for the equally good results obtained with 95 per cent and absolute alcohol.

The chlorination reaction is exothermic, and the best results are obtained by permitting the temperature to rise to 80 to 90°, corresponding to the reflux temperature of ethanol, and then operating at that temperature by regulation of the chlorine feed and heat delivered to the jacket or internal coils of the reaction vessel. The reaction product, which is a clear, yellow, viscous oil (sp. gr., 1.50 to 1.55), is carefully mixed with an equal quantity of 80 to 95 per cent sulfuric acid and then distilled. The fraction boiling between 95 to 98° is taken as the chloral cut. When 90 to 95 per cent acid is used, no hydrate distills over but some charring occurs. When 70 to 80 per cent sulfuric acid is employed, the distillate is a mixture of chloral and chloral hydrate. Such a mixture can, however, be used for the manufacture of DDT (see technical section) by condensation with chlorobenzene in the presence of sulfuric acid.

Aliphatic Acids.—By the appropriate choice of chlorinating agents, aliphatic carboxylic acids can be converted either to chloro derivatives by substitution of H in the alkyl chain or to acid chlorides by replacement of the —OH of the carboxyl group (see pages 219, 220).

Chloro-carboxylic Acids.—The chlorination of liquid aliphatic carboxylic acids generally takes place at temperatures lower than are necessary for paraffins. A diversity of procedures and catalysts have been employed for the preparation of such compounds. When chlorine gas is the chlorinating agent, iodine, sulfur, phosphorus, and their halides can be used as catalysts.

Chloroacetic acid can be prepared by passing the requisite quantity of chlorine into a vessel containing 200 parts of acetic acid, 5 parts of red phosphorus, 1 part of iodine, and 5 parts of phosphorus pentachloride at 100°. By elevating the temperature to 160° and adding additional chlorine, it is feasible to produce trichloroacetic acid.

As is shown later on page 222, sulfuryl chloride, in the presence of an organic peroxide, can also be effectively used for the preparation of chloro aliphatic carboxylic acids, their alkyl esters, and chloroacyl halides.

Tetra- and pentachloroethanes can also be employed for the preparation of mono- and dichloroacetic acids, respectively. The hydrolytic reactions, which are carried out in sulfuric acid, may be represented as follows:[1]

$$CH_2Cl{\cdot}CCl_3 + 2H_2O \xrightarrow{H_2SO_4} CH_2Cl{\cdot}COOH + 3HCl$$
$$CHCl_2{\cdot}CCl_3 + 2H_2O \xrightarrow{H_2SO_4} CHCl_2{\cdot}COOH + 3HCl$$

The water is supplied by sulfuric acid of 90 to 95 per cent strength. The preparation of dichloroacetic acid is accomplished by intimately mixing 1,400 parts of pentachloroethane and 1,000 parts of 93 per cent sulfuric acid at 168°C. A regular evolution of hydrogen chloride occurs particularly when additional dilute sulfuric acid is introduced to compensate for the loss of water entering into reaction. The reaction mixture is distilled *in vacuo;* whereby the unreacted pentachloroethane is first removed, and this is followed by the fraction consisting of relatively pure concentrated dichloroacetic acid.

Chlorination in the Side Chain of Aromatic Compounds.—When chlorine is passed into boiling toluene in the presence of natural or artificial light, a mixture of different chlorine products is obtained. The degree of halogenation will depend on the quantity of chlorine consumed, the principal products being those in which chlorine is substituted in the side chain; but compounds containing chlorine in the ring are also present.

Generally, a higher temperature of chlorination favors substitution in the side chain, while chlorination at a lower temperature in the presence of a catalyst, *e.g.*, iron, favors the replacement of nuclear hydrogen. On mixing gaseous toluene in excess, with chlorine gas in the presence of light, only a portion of the hydrocarbon is converted. Benzyl chloride, benzal chloride, and benzotrichloride, as well as chlorotoluene and chlorobenzyl chloride, etc., are produced.

When chlorine gas and vapors of toluene in definite stoichiometric proportions are permitted to react in the presence of ultraviolet rays, the formation of side-chain compounds in a comparatively pure condition is favored. One mole of chlorine (35.5×2) is required for the substitution of each hydrogen atom, the formation of benzyl chloride taking place according to the following reaction:

$$C_6H_5{\cdot}CH_3 + Cl_2 \rightarrow C_6H_5{\cdot}CH_2Cl + HCl$$

For the formation of benzal chloride and benzotrichloride, 2 and 3 moles, respectively, will obviously be required.

The preparation of these side-chain halides can be carried out in the vapor phase as follows:[2] A reaction chamber, lined with bonded lead, is provided with a quartz mercury lamp, which emits ultraviolet rays. Liquid toluene is delivered to a vaporizer, and the gaseous hydrocarbon is drawn into the reaction chamber. The chlorine, in calculated quantities based on the toluene used, is delivered through a measuring apparatus directly into the reaction chamber by means of a tube concentric with that employed for delivering the toluene vapors. The product of the reaction collects at the bottom of the chlorination chamber and is drawn off in such a manner as to prevent the introduction of air. The hydrogen chloride formed is drawn off through the top of the chamber. This operation is preferably performed at 130 to 140°C., a temperature below the boiling point of the side-chain halide.[1] In this way, benzyl chloride (b.p., 179°C.) is removed from the gaseous reaction sphere, and its further chlorination is inhibited.

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[1] U. S. 2,036,137 (1936).

[2] Gibbs and Geiger, U. S. 1,246,739 (1917)

When hot toluene at 80 to 100°C. is allowed to trickle through a tall vitreous tower packed with glass rings, countercurrent to the supply of chlorine, the chlorination to benzyl chloride can be made to take place in the liquid phase.[2] The reaction is carried out in a glass tower which is equipped with mercury lamps spaced every 4 ft. to ensure uniform illumination. Hot toluene is introduced continuously and in a regulated flow into the top of the tower, and dry chlorine is delivered at the bottom. The rate of feed is adjusted to keep the temperature below the boiling point of toluene (111°C.). The benzyl chloride is withdrawn at the base, while the hydrogen chloride, along with some hydrocarbon vapors, is removed at the top. Through the introduction of a cooler and scrubber, the toluene can be condensed and returned with fresh material.

Chlorination in the Nucleus of Aromatic Compounds.—Substitution of chlorine for hydrogen in the benzene ring takes place readily. The reaction is greatly facilitated by the presence of a halogen carrier, such as iron, aluminum, or iodine. Previously, it has been shown that side-chain chlorination occurs with the alkylbenzenes when chlorination is carried out at comparatively elevated temperatures and in the presence of light. At low temperatures and in the presence of a halogen carrier, if reaction takes place, the halogen replaces hydrogen atoms in the ring.

Chlorination of Benzene.—The chlorination of benzene is carried out in iron vessels which may be lined with lead or coated with glass. Steel or wrought-iron particles which are gradually converted to anhydrous ferric chloride are generally used as the halogen carrier. The reaction vessel is provided with an efficient stirrer and a reflux condenser. Benzene takes up chlorine readily in the presence of a carrier, and the heat of the reaction brings the charge to boil, making it necessary to employ a cooling or refluxing system to control the temperature. When only monochlorobenzene is desired, it is advisable to maintain the temperature at 40°C. and use only about 60 per cent of the chlorine necessary for

[1] Ger. 478,084 (1929).

[2] Conklin, U. S. 1,828,858 (1931).

chlorination. When chlorine is passed in until the increase in weight indicates that the theoretical quantity of chlorine, calculated for monochlorination, has been consumed, some dichlorination takes place, and the charge will give approximately the following fractions when rectified in a column:

Distillation products	%	Boiling range, °C.
Benzene	3	79 to 81
Benzene and chlorobenzene	10	81 to 125
Chlorobenzene	75	126 to 133
Chlorobenzene and dichlorobenzenes	10	133 to 180
Resinous materials and loss	2	

The yield of monochlorobenzene decreases slightly as the temperature of chlorination is raised. In the vicinity of ordinary temperatures (18 to 35°C.) for every 10° rise, the temperature coefficient of the velocity of transformation of the mono- to dichlorobenzenes is about 8.5 per cent higher than that of the transformation of benzene to chlorobenzenes.[1] Hass has made similar observations with respect to the vapor-phase chlorination of paraffins and reasonably attributes the phenomenon to the tendency of the energy-rich freshly formed monochloride to react with more chlorine when it is present in high concentrations.[2]

Vapor-phase Chlorination of Benzene.—Chlorine reacts with excess of benzene at temperatures above 400°C. to yield mono- and dichlorobenzenes, with little or no trichlorobenzene.[3] When the molecular proportion of benzene to chlorine falls below 1:1, inflammation occurs at the entrance to the reaction tube but can be stopped by momentarily increasing the flow of benzene.

The data in Table VII show that there is little change in the ratio of mono- and dichlorobenzenes with change in the temperature of reaction. It is evident that for a given space velocity, there is a critical temperature below which the amount of chlorine passing through unreacted increases rapidly. Above certain temperatures, pyrolysis sets in and carbon is deposited. In Fig. 7 are compared the experimental results with the theoretical curves for a two-stage (possible bimolecular reactions) process. It is apparent that the experimental and calculated results are in close agreement.[4]

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[1] Bourion, *Compt. rend.*, **170**, 1319 (1920).

[2] Hass, *Ind. Eng. Chem*, **29**, 1338 (1937).

[3] Mason *et al.*, *J. Chem. Soc.*, **1931**, 3150.

[4] Martin and Fuchs, *Z. Elektrochem.*, **27**, 150 (1921).

TABLE VII.—EFFECT OF VARYING TEMPERATURE: VAPOR-PHASE CHLORINATION OF BENZENE

Molar Ratio, $Cl_2:C_6H_6 = 1:2.2$

Tube Diameter, 2.0 Cm. Space Velocity, 10 per Min.†

°C.	Percentage of benzene introduced converted into			Unreacted chlorine, % of input
	C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_3Cl_3$	
500	31.3	2.7	Nil	Nil*
475	32.6	3.5	Nil	Nil*
450	34.5	3.2	Nil	Nil
425	32.9	3.9	Nil	0.1
400	32.5	3.9	Nil	1.0
375	24.1	2.1	1.0	20.1

* Carbon deposited.

† Space velocity, *i.e.*, the number of volumes of gas, at the reaction-tube temperature, passing through the heated volume per minute.

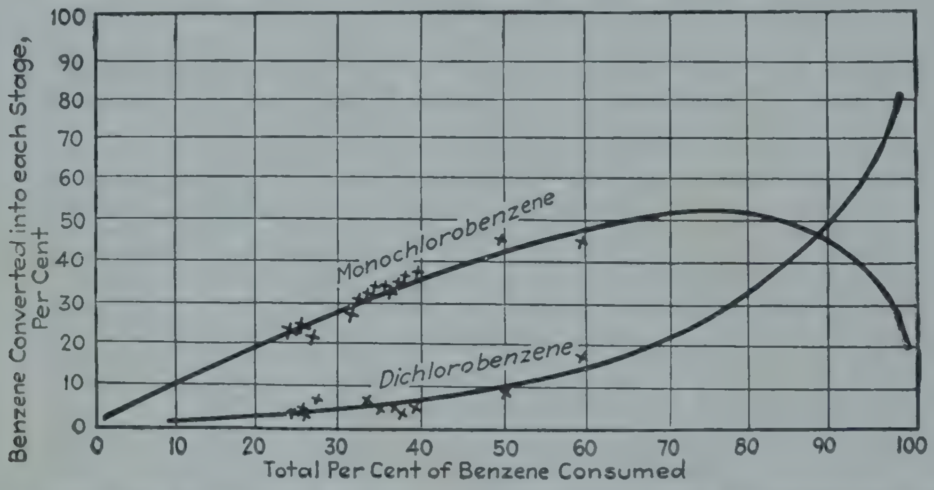

FIG. 7.—Vapor-phase chlorination of benzene. Continuous curves = theoretical curves for two-stage reaction. Points marked x = experimental values.

Chlorination of Naphthalene and Biphenyl in Presence of a Solvent.—In organic synthesis, it is often necessary, in carrying out reactions, to employ inert solvents or solvents that, although normally reactive, will remain substantially inert under the conditions of reaction employed. Thus, Britton has shown that benzene can advantageously be employed as a solvent in the chlorination of naphthalene and biphenyl.[1]

α-Chloronaphthalene can thus be prepared by taking 150 parts by weight of naphthalene and 300 parts of benzene and passing in chlorine in the presence of iron until about 0.8 mole of chlorine is absorbed. The hydrogen chloride remaining in solution is neutralized by adding soda ash, and any excess of the latter together with the resulting sodium chloride is separated by filtration or decantation. On distillation of the filtrate, about 95 per cent of the benzene employed is recovered. A yield of about 85 per cent technical α-chloronaphthalene based on naphthalene consumed is obtained.

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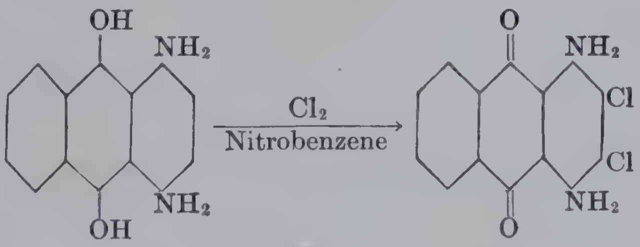
[1] Britton, U. S. 1,784,267 (1930); U. S. 1,835,754 (1931).

Halogenation of Anthraquinones.—Ordinarily, the halogenated anthraquinones are derived from the corresponding keto acids, which in turn are prepared according to the Friedel-Crafts reaction. Thus, not only chlorobenzene but also *o*- and *m*-dichlorobenzenes have been utilized in the synthesis of halogenated keto acids by condensing with phthalic anhydride as well as its halogen derivatives. Under certain conditions, particularly when halogeno-amino derivatives are required, it is desirable to chlorinate the anthraquinone compounds directly in order to obtain a specific intermediate for vat dye manufacture.

The chlorination of 2-aminoanthraquinone can be carried out by suspending 10 parts of the amine in 100 parts of nitrobenzene and then passing in chlorine until the increase in weight indicates monochlorination. With constant agitation, the mixture is boiled vigorously for ½ hr. and then permitted to stand overnight. The 2-amino-3-chloroanthraquinone that crystallizes out is filtered off and washed with nitrobenzene, alcohol, and finally water. When 20 parts of 2-amino-3-chloroanthraquinone is suspended in 180 parts of nitrobenzene containing 10 parts of sodium carbonate and treated with 21 parts of bromine dissolved in 60 parts by weight of nitrobenzene, the bromine enters the alpha position. The 1-bromo-2-amino-3-chloroanthraquinone thus obtained is isolated by the procedure previously used.

An aminoanthraquinone can also be chlorinated in nitrobenzene solution if it is first converted to the leuco compound. Upon oxidation, the chlorinated aminoanthraquinone is obtained.



Carbon Tetrachloride: Chlorination of Carbon Disulfide.—The fundamental reaction of carbon disulfide with chlorine may be expressed as follows:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2 \qquad (1)$$

This reaction readily goes to completion and is an economic procedure for the manufacture of carbon tetrachloride when the demand for sulfur monochloride is sufficient. When the demand for both products is not in balance, it is desirable to employ the sulfur monochloride as a chlorinating agent in accordance with the following reversible reaction:

$$CS_2 + 2S_2Cl_2 \rightleftharpoons 0.2CS_2 + 0.4S_2Cl_2 + 0.8CCl_4 + 4.8S \tag{2}$$

Instead of chlorination of the carbon disulfide with elemental chlorine or sulfur monochloride as indicated above, sulfur dichloride may be used in accordance with the following equation:

$$CS_2 + 6SCl_2 \rightarrow CCl_4 + 4S_2Cl_2 \tag{3}$$

This reaction readily goes to completion, but here also sulfur monochloride is a by-product. When an effort is made to diminish the formation of sulfur monochloride in accordance with Eq. (4), the reaction, like Eq. (2) above, does not go to completion.

$$CS_2 + 2SCl_2 \rightleftharpoons 0.1CS_2 + 0.2S_2Cl_2 + 0.9CCl_4 + 3.4S \tag{4}$$

The reaction between carbon disulfide and sulfur monochloride can be carried out so as to leave no unreacted S_2Cl_2 by the use of an excess of CS_2 as follows:

$$3CS_2 + 4S_2Cl_2 \rightleftharpoons 2CCl_4 + 12S + CS_2 \tag{5}$$

To obviate difficulties in separating the carbon tetrachloride from sulfur dichloride (b.p., 59°), it is customary to use reactions (1) and (5) alternately. Part of the carbon tetrachloride (b.p., 76.74°) is distilled after reaction (1), and the residual sulfur monochloride (b.p., 138°) is transferred and treated in accordance with Eq. (5). When the carbon disulfide and carbon tetrachloride which are recycled to reaction (1) are distilled, all the liberated elemental sulfur is removed. During this distillation, some reversal occurs.

CCl_4: *Other Methods of Preparation.*—Carbon tetrachloride can be made by the direct chlorination of methane,[1] and success in such operations depends on removing the large heat of reaction. This can be accomplished by employing a tall cylindrical reactor which is divided into sections to permit regulation of temperatures. Appropriate mixtures of activated carbon (as catalyst) and graphite (as heat conductor) are used on each section so as to obtain moderate conversion and high heat transfer at first and complete conversion at the exit end of the chlorinator. Carbon tetrachloride can also be obtained by the reaction of chlorine with perchloroethylene.

$$2Cl_2 + C_2Cl_4 \rightleftharpoons 2CCl_4$$

The latter process can be carried out in a continuous manner in the vapor phase and is devoid of the problems of removing sulfur attending the chlorination of carbon disulfide. When perchloroethylene and chlorine are simultaneously passed through a chamber heated to 700 to 800°, carbon tetrachloride is formed and can be continuously separated in a fractionating column provided with a dephlegmator.[1]

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[1] Pie, U. S. 2,280,928 (1942).

Addition Reactions.—The olefins combine readily with chlorine and bromine. In these reactions, the characterizing double bond is replaced by a single bond, and two halogen atoms become attached to the adjacent carbon atoms which were previously united by a double bond:

$$\begin{aligned}&CH_3{\cdot}CH{=}CH_2 + Cl_2 \rightarrow CH_3{\cdot}CHCl{\cdot}CH_2Cl\\&CH_3{\cdot}CH{=}CCl_2 + Cl_2 \rightarrow CH_3{\cdot}CHCl{\cdot}CCl_3\end{aligned}$$

The addition reactions are usually carried out in the presence of a solvent that may be some of the finished product or unwanted higher chlorinated derivatives. Any of the lesser active polychlorinated compounds such as CCl_4 and $C_2H_2Cl_4$ may also be used.

When the hydrogen halides are similarly allowed to react with olefinic hydrocarbons, the halogen, in accordance with Markownikoff's rule, ordinarily attaches itself preponderantly to that carbon with which are combined the least number of hydrogen atoms, while the hydrogen adds on to the terminal carbon atom.

$$\begin{aligned}&CH_3{\cdot}CH{=}CH_2 &+ HCl \rightarrow CH_3{\cdot}CHCl{\cdot}CH_3\\&CH_3{\cdot}CH_2{\cdot}CH{=}CH_2 &+ HCl \rightarrow CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3\end{aligned}$$

If this reaction were universally true, only secondary and tertiary halogeno compounds could be obtained from the higher olefins. Kharasch has, however, shown (see page 228) that the addition of HBr to the double bonds of olefinic hydrocarbons is influenced by the presence of either peroxides or antioxidants, the former serving to produce primary and the latter secondary or tertiary halogen derivatives.[2]

In the chapter on Hydrolysis, it is shown that when a mixture of olefins is treated with sulfuric acid, the butylenes and propylene will react under milder conditions of temperature, pressure, and acid concentration than ethylene. Similarly, it is feasible to effect the selective chlorination of the higher olefins and, after separation of the liquid chloropropanes, butanes, etc., to chlorinate the residual ethylene.

Preparation of Ethylene Dichloride.—The addition of chlorine to ethylene may be effected in the liquid phase in the presence of a cosolvent or in the vapor phase in the presence of metal contact agents.

The use of solvents ordinarily leads to considerable substitution as well as addition, even at relatively low temperatures. From 10 to 20 per cent polychloroethanes are obtained when operating at 0 to 40°. The cosolvent may be some of the desired product, *viz.*, dichloroethane or dibromoethane or a polychlorohydrocarbon, which can be recovered and reused.

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[1] Wimmer, U. S. 2,305,821 (1942).

[2] KHARASCH, *J. Am. Chem. Soc.*, **55**, 2468, 2521, 2531 (1933); **56**, 244, 712, 1212, 1643, 1782 (1934); **57**, 2463 (1935); **59**, 195 (1937).

According to Hammond, the addition of relatively small amounts (0.05 to 0.25 per cent, based on the weight of dichloroethane used as a cosolvent) of anhydrous ferric chloride will serve to depress substitution reactions.[1] The reaction can be carried out in the apparatus shown in Fig. 8. Chlorine and ethylene, under moderate pressure, are introduced into a reactor containing a body of dichloroethane and provided with a plurality of tubes through which cooling water is circulated. Ferric chloride may be introduced as such but, because of its hygroscopicity, may be first dissolved in anhydrous ethanol or delivered to the reactor with the replacement dichloroethane.

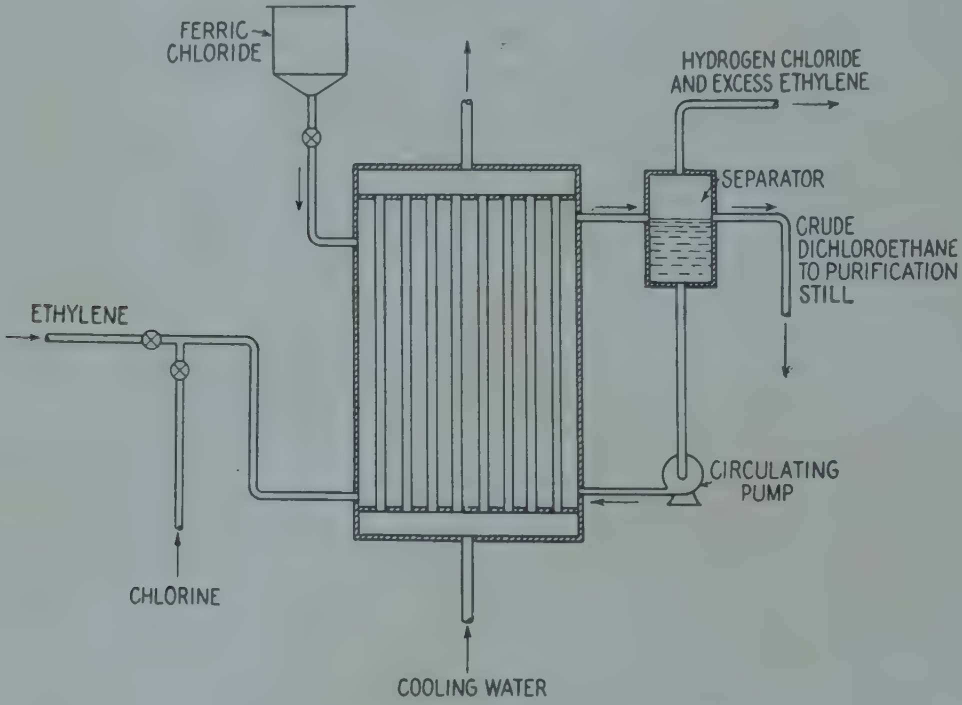
FERRIC CHLORIDE
HYDROGEN CHLORIDE AND EXCESS ETHYLENE
SEPARATOR
CRUDE DICHLOROETHANE TO PURIFICATION STILL
ETHYLENE
CIRCULATING PUMP
CHLORINE
COOLING WATER

FIG. 8.—Manufacture of dichloroethane.

When ethylene and chlorine in a mole ratio of 1.1:1 are reacted in a liquid bath of dichloroethane, maintained at a temperature of 40°C., about 85.6 per cent of the chlorine reacts by addition, and about 7.7 per cent reacts to form higher chlorination products.[1] If, however, the preceding reaction is carried out in the presence of 0.05 to 0.25 per cent of ferric chloride—based on dichloroethane—97.2 per cent of the chlorine reacts by addition to yield dichloroethane, while only 1.75 per cent enters into substitution reactions.

When the addition of chlorine to ethylene is carried out in the vapor phase and in the presence of metal contact agents, higher proportions of 1, 2-dichloroethane are obtained. Equimolecular proportions of chlorine and ethylene reacting at 80 to 100° in the presence of copper or iron give about 90 to 95 per cent of the theoretical yield of dichloroethane. The reaction may be carried out in tubes that are packed with shavings or particles of the preferred metal. When small amounts of dichloroethane are recirculated to the reaction zone, the exit gases can be scrubbed more easily. In many plants, the concurrent formation of polychloroethanes is considered desirable, for such compounds are subsequently submitted to dehydrochlorination and yield desired chloroolefins.

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[1] Hammond, U. S. 2,393,367 (1946).

The chloroolefins behave like olefins and add chlorine or hydrogen chloride. The presence of a metal halide, *e.g.*, ferric or stannic chloride, facilitates liquid-phase reactions. In this way, 2, 2, 3-trichlorobutane is obtained from 2-chlorobutene-2.[1]

$$CH_3CH{=}CClCH_3 + Cl_2 \rightarrow CH_3CHClCCl_2CH_3$$

2. Chlorination by the Action of Hydrochloric Acid with and without Oxidants

Reactions in this group include chlorination with (1) hydrochloric acid and (2) chlorides and chlorates in the presence of mineral acids. The syntheses made possible by the action of hydrochloric acid and generated chlorine comprise reactions involving *addition*, *substitution*, and *replacement*.

Addition Reactions. *Preparation of Alkyl Halides from Olefins.*—There are two general methods for the synthesis of alkyl halides: (1) by the interaction of an alcohol with a halogen hydride—a procedure that may reasonably be discussed under esterification or halogenation and, also, under the Friedel and Crafts synthesis when a metal halide is used to catalyze the reactions—and (2) by the addition of a halogen hydride to an unsaturated hydrocarbon. This reaction may be catalyzed by metal halides and by sulfuric acid. In the latter instance, the ethylsulfuric acid first formed is converted to the halide by gaseous chlorine or chlorine[2] liberated *in situ* by the action of sulfuric acid on a halide.

It has long been known to students of the Friedel and Crafts reaction that olefins could be employed instead of the corresponding alkyl halides in alkylation reactions, since they were transformed into the alkyl halide by the added or liberated halogen hydride. The preparation of the alkyl halide may be presented as follows:

$$R{-}HC{=}CH_2 + HCl \xrightarrow[\text{Catalyst}]{\text{Friedel and Crafts}} R{-}CHCl{\cdot}CH_3$$

---

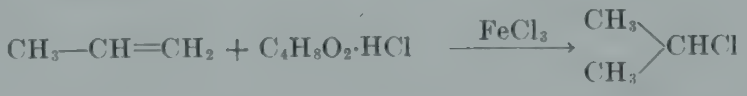
[1] Levine and Cass, U. S. 2,323,227 (1943).

[2] U. S. 2,016,072 (1935).

Aluminum chloride,[1] ferric chloride,[2] bismuth trichloride,[3] zinc chloride,[4,5] and stannic chloride[6] have been variously employed to catalyze the reaction.

The synthesis may be carried out as a batch process by bringing the olefin and halogen hydride together, in a pressure vessel containing the catalyst (*a*) suitably distributed over an absorbent material or (*b*) dissolved in an inert solvent. The synthesis may also be effected by passing the reactants as vapors over a solid catalyst; *e.g.*, zinc chloride on charcoal at approximately 100°C.

Instead of hydrogen chloride, the addition compound of dioxane and hydrochloric acid ($C_4H_8O_2 \cdot HCl$) can be employed.[7] The complex forms in the presence of water, and aqueous solutions of the hydrogen halides may thus be used in its preparation. Approximately 41.7 gm. of hydrogen chloride combines exothermally with 100 gm. of dioxane, and the resulting compound forms crystals at about −40°. The addition compounds when used in greater than mole-for-mole proportions as shown in the equation below, can be effectively used to convert propylene to isopropyl chloride.



$$CH_3{-}CH{=}CH_2 + C_4H_8O_2 \cdot HCl \xrightarrow{FeCl_3} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CHCl$$

Another modification of this process is the use of metal halide addition compounds in order to moderate the reaction and prevent excessive polymerization of the reacting olefins. The complex derived from aluminum chloride and diethyl ether is used advantageously for the preparation of pentyl chloride from pentene-2.[8]

In general, the ease of synthesis of alkyl halides from olefins is dependent on the molecular weights of the hydrocarbons and the particular hydrogen halide. Thus, as was explained earlier in this chapter, the reaction becomes more difficult in passing from iodides through bromides to chlorides. Likewise, olefins containing several carbon atoms react much more readily than those of a lower order.

Preparation of Chloroolefins and Diolefins by Hydrochlorination.—When a gaseous mixture of acetylene and hydrogen chloride is passed through a reaction chamber packed with highly activated charcoal or silica gel impregnated with a solution containing about 20 per cent calcium chloride, 10 per cent barium chloride, and 1 per cent mercuric chloride[1] or mercurous chloride,[2] vinyl chloride is obtained.

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[1] U. S. 1,518,182 (1924).

[2] U. S. 1,637,972 (1927).

[3] U. S. 1,591,151 (1926).

[4] U. S. 2,094,064 (1937).

[5] U. S. 2,097,750 (1937).

[6] U. S. 2,099,480 (1937).

[7] Thomas and Morris, U. S. 2,285,473 (1942).

[8] Waterman and Leendertse, U. S. 2,280,207 (1942).

$$HC{\equiv}CH + HCl \xrightarrow[200^\circ]{\substack{HgCl_2 \\ \text{Impregnated Charcoal}}} CH_2{=}CHCl$$

Vinylacetylene can be hydrochlorinated in a continuous manner in the presence of an aqueous cuprous chloride solution. The principal reaction is the formation of chloroprene, 2-chlorobutadiene-1, 3.

$$HC{\equiv}C{-}CH{=}CH_2 + HCl \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CCl{-}CH{=}CH_2$$

A secondary reaction involving the formation of 1, 3-dichlorobutene-2 occurs concurrently.

$$H_2C{=}CCl{-}CH{=}CH_2 + HCl \rightarrow CH_3{-}CCl{=}CH{-}CH_2Cl$$

To obtain high yields of chloroprene, the circulation rate of vinylacetylene through the reaction zone needs to be great, and it must be used in excess of the rate at which it is consumed. The aqueous solution containing hydrogen chloride, cuprous chloride, and ammonium chloride passes downward through the reactor maintained at 40 to 65° and reacts with the rising vinylacetylene vapors. The used hydrogen chloride solution is freed of tars, fortified with fresh hydrogen chloride, passed through a column packed with copper particles, and then recirculated to the reaction zone.[3]

In the following section dealing with the Preparation of Chloroolefins by Dehydrohalogenation, it is shown that such compounds can be made either by chlorinating olefins with gaseous chlorine at a critical temperature range or by catalytic or thermal dehydrochlorination. Cass has shown that a mixture of hydrogen chloride and oxygen can be successfully substituted for elemental chlorine in the preparation of chloroolefins.[4] The reactions that take place may be represented by the following equations:

$$\begin{array}{llllll}
CH_2{=}CH_2 & + \; HCl & + \; \tfrac{1}{2}O_2 & \rightarrow CH_2{=}CHCl & + \; H_2O & (1)\\
CH_2{=}CH_2 & + \; 2HCl & + \; O_2 & \rightarrow CHCl{=}CHCl & + \; 2H_2O & (2)\\
CH_2{=}CH_2 & + \; 4HCl & + \; 2O_2 & \rightarrow CCl_2{=}CCl_2 & + \; 4H_2O & (3)\\
CH_2{=}CHCl & + \; 2HCl & + \; O_2 & \rightarrow CHCl{=}CCl_2 & + \; 2H_2O & (4)
\end{array}$$

$$CHCl{=}CHCl + 2HCl + O_2 - \!\!\begin{array}{l} \nearrow CHCl{=}CCl_2 + H_2O \\ \searrow CCl_2{=}CCl_2 + 2H_2O \end{array} \qquad (5)$$

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[1] Schaeffer, U. S. 2,338,459 (1944). See also U. S. 2,328,430; 2,329,795 (1943).

[2] Lazier and Whitman, U. S. 2,391,465 (1945).

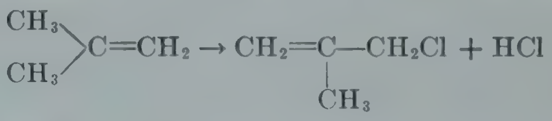
[3] Carter and Downing, U. S. 2,221,941 (1940).

[4] Cass, U. S. 2,308,489; 2,327,174 (1943); 2,342,100 (1944); 2,374,923; 2,379,414 (1945).

The use of an oxidation catalyst is essential (Deacon process) in order to obtain satisfactory results. Good yields are obtained by using firebrick saturated with cupric oxide, nitrate, etc. It is important to operate in a relatively narrow critical range (400 to 450°) in which chlorination and dehydrochlorination reactions can occur concurrently. When the chlorination temperature is sufficiently lowered, addition reactions predominate. When the temperature is too high, the yields are low because of pyrolytic reactions which are accompanied by the liberation of carbon oxides.

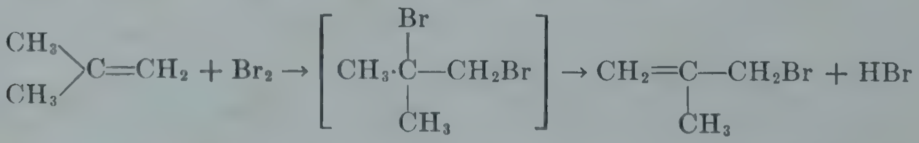
Even under carefully controlled conditions, a diversity of reaction products are obtained in such "substitutive" chlorinations. Thus, when 10.3 moles of vinyl chloride, 20.9 moles of hydrogen chloride, and 15.5 moles of oxygen (as air) are passed over a copper oxide catalyst at 400 to 460°, the gas effluent consists of 0.89 mole dichloroethylene, 2.12 moles trichloroethylene, and 3.35 moles perchloroethylene. More or less saturated chloroparaffins are formed, depending on the temperature of reaction.

Under certain conditions, it appears that the chlorinated olefin can be obtained directly by substitutive methods; *e.g.*, methallyl chloride is obtained when isobutylene (2-methyl-1-propene) is treated with an insufficient quantity of chlorine for less than 1 sec., and the hot reaction gases at about 300°C. are then passed into a scrubbing tower containing dilute hydrochloric acid.[1] The initial and final products are



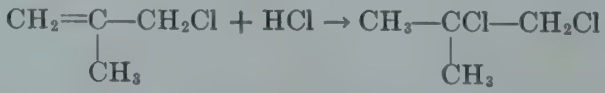
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C{=}CH_2 \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2Cl + HCl$$

There is no evidence for the formation of the expected intermediate dichloride although it is known that the bromine adds on in a normal fashion to give a yield of 75 per cent isobutylene dibromide which would yield the methallyl bromide on dehydrohalogenation.



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C{=}CH_2 + Br_2 \rightarrow \left[CH_3{\cdot}\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2Br\right] \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2Br + HBr$$

It is also known that methallyl chloride adds HCl in the expected manner to give isobutylene dichloride, thus:



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2Cl + HCl \rightarrow CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CCl}}{-}CH_2Cl$$

Substitution Reactions. *Chlorination of Methane with Hydrogen Chloride in the Presence of Oxygen.*—It has been shown that the introduction of air or oxygen into the reaction chamber containing chlorine and methane makes possible the conversion of the liberated hydrogen chloride to active chlorine. Thus, methyl chloride can be made by first chlorinating methane with gaseous chlorine in the vapor phase and then employing the liberated hydrogen chloride and oxygen in an integrated catalytic conversion zone for the further chlorination of methane.[1]

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[1] U. S. 2,077,382 (1937).

$$2CH_4 + 2Cl_2 \rightarrow 2CH_3Cl + 2HCl$$
$$2CH_4 + 2HCl + O_2 \xrightarrow[400^\circ C.]{Cu_2Cl_2} 2CH_3Cl + 2H_2O$$

The second stage of the process may be carried out as follows:[2] A mixture of two volumes of methane and one of hydrogen chloride is led into a tube containing pumice impregnated with cupric chloride and brought to a temperature of 400°C. The reaction tube is of sufficient length to ensure a practically complete transformation of the hydrogen chloride. The exit gases from the catalytic chamber are cooled to remove water and hydrochloric acid. The chlorinated methane is washed to remove any residual acid and then recovered either by absorption in a high-boiling solvent or by cooling and employing pressure.

The residual gases, comprising methane and oxygen, may be returned to the catalytic chamber along with more hydrogen chloride, oxygen, and methane. When air is employed instead of oxygen, the reaction proceeds more slowly on account of the presence of such a comparatively large volume of nitrogen. Under such circumstances, it is advisable to employ a second catalytic chamber into which additional air and hydrogen chloride are added to combine with the unchlorinated methane.

Thus far, the oxidation-chlorination technic has not been found practical when applied to methane. The oxygen and the liberated steam cause extensive oxidation and hydrolysis.

Benzene, however, is successfully chlorinated by an entirely similar procedure.[3] Vapors of benzene and hydrogen chloride in the ratio of 600 to 300 parts by volume are mixed with 170,000 volumes of air and led into the catalytic chamber containing pumice impregnated with cupric chloride or preferably a mixture of cupric and ferric chlorides at 180°C. The condensed reaction gases separate out into a two-layer liquid system, comprising dilute hydrochloric acid and chlorobenzene. The chlorobenzene layer is washed free of acid and then submitted to fractional distillation. Only a small quantity of benzene and higher chlorinated compounds is found to accompany the principal product. For the practical application of this procedure as the first step in the technical production of phenol, see Chap. XI, Hydrolysis.

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[1] Riblett, U. S. 2,334,033 (1943).

[2] U. S. 1,654,821 (1928); Ger. 486,952 (1929).

[3] Ger. 487,596 (1929); U. S. 1,935,648 (1933); U. S. 1,963,761 (1933).

Manganese dioxide may be used as the oxidant when the chlorination of benzene takes place in the liquid phase. Under such circumstances, the hydrogen chloride may be liberated *in situ* by the action of sulfuric acid on sodium chloride. The reactions involved are

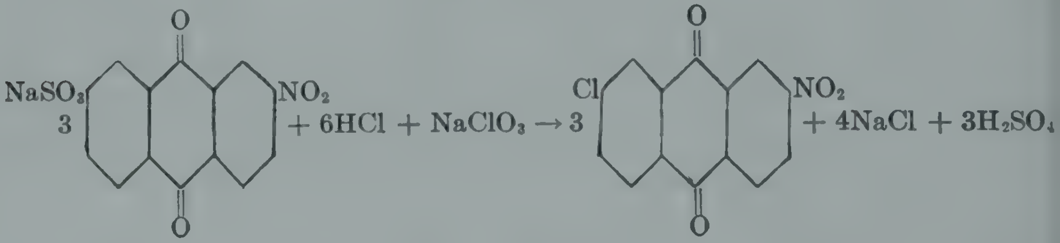
$$C_6H_6 + MnO_2 + 3HCl \rightarrow C_6H_5Cl + MnCl_2 + 2H_2O$$
$$C_6H_6 + MnO_2 + 2H_2SO_4 + NaCl \rightarrow C_6H_5Cl + MnSO_4 + NaHSO_4 + 2H_2O$$

Hydrogen chloride also adds to unsaturated fluoroolefins in accordance with the following reaction:[1]

$$CF_2{:}CF_2 + HCl \rightarrow CHF_2{\cdot}CF_2Cl$$

Preparation of Chloroanthraquinones. Replacement of Sulfonic Acid Groups.—The sulfonic acid groups of anthraquinone compounds can readily be replaced by chlorine. Hydrochloric acid or liberated hydrogen chloride may be used as the source of chlorine. The reaction is generally carried out in the presence of compatible oxidants such as chlorates and chlorites.

When 2-nitroanthraquinone-7-sulfonic acid, for example, is thus treated, the β-sulfonic acid group is replaced. The following equation probably best represents the reaction:[2]



Instead of hydrochloric acid, it is feasible to employ sodium chloride and sulfuric acid in the presence of chlorates. The required chlorine is thereby liberated *in situ*. It is possible, furthermore, to utilize the sulfuric acid solution resulting from the preparation of the sulfonic acid derivatives. Such a procedure provides a convenient and economical method for recovering and utilizing any disulfonates that remain in solution after the less soluble and comparatively pure monosulfonate has been isolated by salting out and filtering.[3]

Utilization of Liberated Hydrogen Chloride. *Preparation of Alkyl Halides.*—By causing the hydrogen chloride split off in direct chlorinations to react with compatible alcohols, it is not necessary to employ oxidants to obtain a maximum utilization of the chlorine introduced. Thus, methanol can be introduced into the chamber containing hydrogen chloride, hydrocarbon, and chlorinated hydrocarbon and is converted (esterified) to methyl chloride. The principal reactions involved may be represented as follows:

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[1] U. S. 2,393,304 (1946).

[2] U. S. 1,810,011 (1931).

[3] U. S. 1,761,620 (1930). The reverse procedure whereby halogen atoms are replaced by the sulfonic acid group through the medium of sulfites is discussed in Chap. V, Sulfonation.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$
$$HCl + CH_3OH \rightarrow CH_3Cl + H_2O$$

When methylene chloride is desired, the reactions are

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$HCl + CH_3OH \rightarrow CH_3Cl + H_2O$$

Chlorination with Hydrochloric Acid. Esterification of Alcohols.—The reactions between alcohols and hydrochloric acid may be represented by the following equation:

$$R{\cdot}OH + HCl \rightarrow R{\cdot}Cl + H_2O$$

It is apparent that the preparation of alkyl chlorides by this method is indeed a process of esterification. The following brief remarks merely present the operation in its relationship to other halogenations: Such reactions are catalyzed by dehydrating agents such as strong sulfuric acid, ethyl hydrogen sulfate, diethyl sulfate,[1] zinc chloride,[2] and copper sulfate. For continuous esterification in the vapor phase, the use of granular alumina gel packed in a converter maintained at 380° gives excellent results.[3]

Preparation of Chloroolefins.—Cass has shown that the use of oxygen in accordance with the Deacon process permits maximum utilization of the halogen in the reaction system in carrying out thermal chlorinations. The function of the oxygen is to convert any hydrogen chloride *formed* or *introduced* into active chlorine. Therefore, one O_2 needs to be used for each 2HCl or $2Cl_2$; water vapor being the coproduct of reaction. The utility of this technic may be exemplified by the following three sets of reactions:

$$CH_2{=}CH_2 + Cl_2 + \tfrac{1}{2}O_2 \rightarrow CHCl{=}CHCl + H_2O \qquad (1)$$
$$CH_2{=}CH_2 + 2Cl_2 + O_2 \rightarrow CCl_2{=}CCl_2 + 2H_2O \qquad (2)$$

If a 10 per cent excess of oxygen is used in reaction (2), the product comprises 5 to 10 per cent dichloroethylene, 25 to 35 per cent trichloroethylene, and 50 to 60 per cent perchloroethylene.[4]

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[1] Green and Hemminger, U. S. 2,308,170 (1943).

[2] Holt and Daudt, U. S. 1,983,542 (1934).

[3] Carlisle, U. S. 1,834,089 (1931).

[4] Cass, U. S. 2,327,174 (1943).

Symmetrical and unsymmetrical dichloroethylene undergo similar reactions;[1]

$$2CHCl{=}CHCl + 2Cl_2 + O_2 \rightarrow 2CCl_2{=}CCl_2 + 2H_2O \tag{3}$$
$$4CCl_2{=}CH_2 + 2Cl_2 + O_2 \rightarrow 4CCl_2{=}CHCl + 2H_2O \tag{4}$$

Previously, it was shown that when chloroalkanes or chloroolefins are subjected to temperatures of 350 to 450°, dehydrochlorination occurs. In the presence of oxygen and an oxidizing catalyst, however, most of the hydrogen chloride is converted to chlorine, which is found in the resultant chloroolefin.

$$2CH_3CH_2Cl + O_2 \rightarrow 2CH_2{=}CHCl + 2H_2O \tag{5}$$
$$2CH_2ClCHCl_2 + O_2 \rightarrow 2CCl_2{=}CHCl + 2H_2O \tag{6}$$

When an excess of 20 per cent oxygen is used in reaction (6), about 25 per cent of the theoretically available hydrogen chloride is found in the reaction products, the balance of the chlorine being organically bound. The products of distillation show the formation of 36.9 mole per cent of trichloroethylene, 21.1 mole per cent dichloroethylene, and 5.7 per cent unconverted beta trichloroethane.[2]

The preceding reactions confirm the observations and postulates of Ewell (see pages 182–185) regarding the equilibrium that exists under certain conditions between halogenation and dehydrohalogenation.

Halogen Exchange.—Alkyl halides and unsaturated aliphatic compounds can simultaneously be obtained by treating halogenated aliphatic carboxylic acids, nitriles, or esters with aliphatic alcohols and/or ethers in the temperature range 260 to 320° and 700 lb. pressure.[3] During the course of the reaction, hydrogen chloride is split out, the hydrogen and chlorine coming from adjacent carbon atoms. Under the conditions of reaction, the hydrogen chloride converts the reacting alcohol to the corresponding halide. The equations underlying such reactions may be expressed as follows:

$$\underset{\beta\text{-Chloropropionic Acid}}{CH_2ClCH_2COOH} + CH_3OH \xrightarrow{Al_2O_3} \underset{\text{Acrylic Acid}}{CH_2{=}CH{-}COOH} + \underset{\text{Methyl Chloride}}{CH_3Cl} + H_2O$$

$$\underset{\substack{\beta\text{-Chloropropionic}\\ \text{Methyl Ester}}}{2CH_2ClCH_2COOCH_3} + CH_3OCH_3 \xrightarrow{AlPO_4} \underset{\text{Methyl Acrylate}}{2CH_2{=}CH{-}COOCH_3} + \underset{\text{Methyl Chloride}}{2CH_3Cl} + H_2O$$

A similar halogen exchange occurs when tetrachloroethane and ethanol (or methanol) react at 280° in the presence of an aluminum oxide catalyst.[4] The products are trichloroethylene and ethyl chloride.

$$CHCl_2{\cdot}CHCl_2 + C_2H_5OH \xrightarrow[280^\circ]{Al_2O_3} CHCl{=}CCl_2 + C_2H_5Cl + H_2O$$

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[1] Cass, U. S. 2,379,414 (1945).

[2] Cass, U. S. 2,342,100 (1944).

[3] Andrussow and Stein, U. S. 2,210,564 (1940), German origin.

[4] U. S. 2,210,563 (1940).

3. Dehydrohalogenation

Halogenated Olefins.—Halogenated olefins can be made by the addition of a halogen or a hydrogen halide to acetylene, but most frequently they are made by the substitutive halogenation of paraffins or the halogenation of olefins by addition and then dehydrohalogenation of the polychloro-paraffins. Alcoholic KOH, alkali and alkali earth hydroxides, and nitrogen bases can be used to effect the fission of hydrogen chloride. The use of metal halides and thermal treatment alone have also been found to be highly effective.

Use of Alcoholic Potash.—The preparation of vinyl chloride, 1,1-dichloroethylene, and perchloroethylene may be represented by the following equations:

$$\begin{aligned}
&CH_2{=}CH_2 + Cl_2 \rightarrow CH_2Cl{\cdot}CH_2Cl \xrightarrow{KOH} CH_2{=}CHCl + HCl\\
&CH_2{=}CHCl + Cl_2 \rightarrow CH_2Cl{\cdot}CHCl_2 \xrightarrow{KOH} CH_2{=}CCl_2 + HCl\\
&CHCl{=}CCl_2 + Cl_2 \rightarrow CHCl_2{\cdot}CCl_3 \xrightarrow{KOH} CCl_2{=}CCl_2 + HCl
\end{aligned}$$

When ethylene dichloride (b.p., 84°C.) is used for the preparation of vinyl chloride, it is treated with dilute potassium or sodium hydroxide at approximately 150°C. in a pressure vessel provided with an agitator. By means of a suitable fractional condensing system, the vapors of dichloroethane are condensed and returned to the reactor, the water of reaction is removed, and the volatile vinyl chloride (b.p., 13.9°) is withdrawn and liquefied in a low-temperature condenser.

When propylene dichloride is treated with an alcoholic solution of potassium hydroxide at ordinary temperatures, alpha-chloropropylene will be formed; but when reacted with alkali hydroxides at relatively high temperatures, the product consists largely of the beta-chloro derivative.

$$CH_3{\cdot}CHCl{\cdot}CH_2Cl \left\langle \begin{array}{l} \xrightarrow{\text{Alcoholic KOH @ 25°C.}} CH_3CH{=}CHCl + HCl \\ \xrightarrow{\text{Aqueous KOH @ 150°C.}} CH_3CCl{=}CH_2 + HCl \end{array}\right.$$

Use of Alkali and Alkali Earth Hydroxides.—Sodium and potassium hydroxides as flakes, in the presence of catalytic quantities of glycols, can be employed for the conversion of chloroparaffins to chloroolefins.

$$\begin{aligned}
&CHCl_2{-}CH_2Cl \xrightarrow[\text{Glycol Polymer}]{NaOH} CH_2{=}CCl_2 + HCl\\
&CH_2Cl{-}CH_2Cl \xrightarrow[\text{Glycol Polymer}]{NaOH} CH_2{=}CHCl + HCl
\end{aligned}$$

When trichloroethane is heated with sodium hydroxide alone to 90°, no reaction is observable; but, when some polyethylene glycol (0.5 per cent) is added, the vapors of asymmetrical dichloroethylene are evolved. The similar reaction leading to the formation of vinyl chloride starts at room temperatures and rises spontaneously to about 60°, at which point it is maintained by cooling devices.[1]

A caustic soda solution can also be used for certain dehydrochlorinations and is particularly effective for the conversion of 2, 3-dichlorobutane to 2-chlorobutene-2.[2]

$$CH_3CHClCHClCH_3 \xrightarrow[\text{25 \% Solution}]{\text{NaOH}} CH_3CH{=}CClCH_3 + HCl$$

Trichloroethylene can be prepared in a continuous manner by treating tetrachloroethane with an aqueous suspension of calcium hydroxide (about 10 per cent) in a packed tower. The portion of the column above the point of introduction of the tetrachloroethane is maintained at a temperature above the boiling point of trichloroethylene in water (73°), but below the boiling point of the chloroparaffin in water (94°). Thus, trichloroethylene vapors may be removed continuously overhead while the spent lime slurry is removed at the base of the column.[3]

$$CHCl_2{-}CHCl_2 \xrightarrow[\text{10 \% Suspension}]{Ca(OH)_2} CHCl{=}CCl_2 + HCl$$

Use of Nitrogen Bases.—Dehydrochlorinations can be catalyzed by nitrogen bases such as trialkylamines, dialkylamines, alkylamines, and their hydrochloride salts as well as by quinoline, piperdine, etc.[4] As a practical matter, it makes little difference whether the free nitrogen base is used or the hydrogen chloride salt is employed, inasmuch as the free base will react initially, at least to some extent, with the liberated hydrogen chloride. The preparation of trichloroethylene from tetrachloroethane is carried out at about 160° in the presence of a nitrogen base and a high-boiling diluent, such as diphenyl oxide. The concentration of the nitrogen base should be from 10 to 40 per cent by weight.

Use of Metal Halides.—Metal halides and particularly zinc and aluminum chlorides have been found to be effective dehydrochlorinating agents. When pentachloroethane is heated with aluminum chloride, tetrachloroethylene is obtained.[5] The pentachlorethane is fed continuously into a mixture of tetrachloroethylene and aluminum chloride (or metal aluminum particles) at 120°. The chloroolefin distills over with hydrogen chloride, and the metal halide becomes converted to an organo aluminum chloride complex of diminishing catalytic activity. Fresh catalyst must consequently be added periodically to maintain high conversion rates.

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[1] Strosacker and Amstutz, U. S. 2,322,258 (1943).

[2] Cass, U. S. 2,291,375 (1942).

[3] Nichols, U. S. 2,369,485 (1945). See also Report No. 188, Office of Publication Board.

[4] Vining, U. S. 2,361,072 (1944).

[5] Wimmer and Mugdan, U. S. 2,249,512 (1941).

Thermal Dehydrochlorinations.—When vapors of polychloroparaffins accompanied by a small amount of chlorine or bromine are heated at elevated temperatures, chloroolefins are obtained by dehydrochlorination.

$$CH_2Cl—CH_2Cl \xrightarrow[300\text{–}370°]{Cl_2} CH_2{=}CHCl + HCl$$

$$CHCl_2—CHCl_2 \xrightarrow[300\text{–}350°]{Cl_2} CHCl{=}CCl_2 + HCl$$

Such thermal reactions can be carried out in a continuous manner. Of considerable technical and theoretical importance is the fact that the presence of chlorine (½ to 1 per cent) or of substances that liberate chlorine ($SOCl_2$, C_2Cl_6) permits dehydrochlorination to occur at relatively low temperatures. Thus, the conversion of ethylene dichloride to vinyl chloride is about 30 per cent at 300°, about 50 per cent at 350°, and about 70 per cent by weight at 370°. Without the addition of chlorine, the conversion at 400° is only 2 per cent; and at 500°, not more than 30 per cent by weight of vinyl chloride is obtained.[1]

The conditions prevailing during such dehydrochlorinations are not unlike those characterizing the vapor-phase "substitutive" chlorination of olefins. The halogen is preferably added to the polychloroparaffin immediately before the entrance of the vapor to the reaction chamber. It is probable that the added chlorine initiates chain reactions that are much faster that the unimolecular thermal decomposition, the comparative activation energies are given on pages 182. A similar situation presumably prevails when olefins are chlorinated at 300 to 400°, at which temperature range there is an equilibrium between chlorination and dehydrochlorination. When chlorine does not accompany the chloroparaffins, the energy-rich condition necessary for dehydrochlorination is obtained at temperatures 100 to 200° higher.

Dehydrochlorination processes can obviously also be used for the conversion of chloroparaffins to olefins and diolefins. Thus butadiene-1,3- can be obtained by passing vapors of 1, 2- or 2, 3-dichlorobutane through (*a*) a molten bath containing equimolecular proportions of aluminum chloride and potassium chloride,[2] (*b*) a borosilicate (Pyrex) tube heated at 450°,[3] or (*c*) a chrome molybdenum cast steel alloy at about 700°.[4]

4. Chlorination with Hypochlorites

Hypohalites in alkaline solution are employed to effect halogenations. Such solutions are particularly effective in preparing halogen addition compounds of acetylene. Ethylene chlorohydrin is also frequently made by reacting gaseous ethylene with hypochlorous acid in aqueous solution. Preferably, the gas is introduced under pressure into a solution of hypochlorite containing a weak acid, boric or carbonic acid. Such weak acids give so low a concentration of H^+ that union of this ion with OCl^- to form HOCl is the predominant reaction. In the presence of strong acids, the following equilibrium

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[1] Mugdan and Barton, U. S. 2,378,859 (1945).

[2] Russell, U. S. 2,207,760 (1940).

[3] Cass, U. S. 2,343,107 (1944).

[4] Cantzler and Krekeler, U. S. 2,243,191 (1941).

$$HCl + HOCl \rightleftharpoons H_2O + Cl_2$$

is shifted to the right, and chlorine water is produced.

a. Addition Reactions. *Preparation of Ethylene Chlorohydrin.*—When ethylene is brought into contact with a hypochlorous acid solution, the principal reaction product is ethylene chlorohydrin:

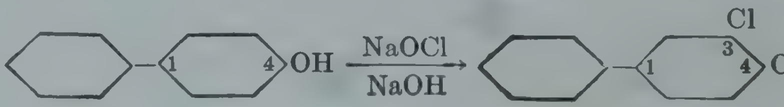
$$HOCl + H_2C{=}CH_2 \rightarrow CH_2OH{\cdot}CH_2Cl$$

Owing to the slight solubility of ethylene in such aqueous solutions at ordinary pressure, some of the undissolved hydrocarbon reacts with the chlorine gas that is present to form ethylene dichloride. To prevent extensive dichloride formation, it is necessary to maintain an excess of ethylene or to increase the solubility of the hydrocarbon by the employment of pressure.

The solubility of ethylene can be increased about two hundredfold by increasing the pressure from atmospheric to 200 atmos. When this property is utilized in the preparation of ethylene chlorohydrin, it is necessary only to bring ethylene gas dissolved in water under high pressure into contact with hypochlorous acid (see page 257).

Instead of pressure, surface active agents can be used to promote the formation of hypochlorous acid and ethylene chlorohydrin.[1] Ethylene is passed at 20 to 30° countercurrent to a hypochlorous acid solution containing sodium lauryl hydrogen sulfate until the concentration of the chlorohydrin is 8 per cent. In addition to the rate of reaction being accelerated, the yield of ethylene chlorohydrin is about doubled, being 77.6 per cent compared with 39.2 per cent for the untreated control.

b. Substitution Reaction. *Chlorination of Hydroxy- or Methoxybiphenyls.*



Alkali hypochlorite solutions can be employed in chlorinating hydroxy- or methoxybiphenyl.[2] One mole of 4-hydroxybiphenyl is dissolved in 1 mole of caustic soda and 6 liters of water. The solution is cooled, and

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[1] Valik, U. S. 2,260,547 (1941).

[2] U. S. 1,832,484 (1931).

1 mole of sodium hypochlorite in solution is added slowly, with constant stirring. The reaction mixture is allowed to stand for about 1 hr. and then warmed to 40°C. After filtration and cooling, 3-chloro-4-hydroxybiphenyl is precipitated by the addition of hydrochloric acid.

Chlorination of Nitroparaffins.—The nitroparaffins are readily chlorinated with alkali hypochlorite solutions. Depending on the ratio of hypochlorite solution, mono-, di-, and trichloro derivatives can be obtained.[1] In practice, the requisite quantity of chlorine is added to a 10 per cent caustic soda solution. It is important to provide an excess of about 20 per cent hypochlorite solution and to maintain the pH between 12 and 14.

The production of chlorpicrin (trichloronitromethane) can be used to illustrate the process. Here, 11.2 parts of nitromethane is added slowly to about 700 parts of a 10 per cent sodium hypochlorite solution under agitation at 20 to 25°. After all the nitromethane has been introduced, stirring is continued until the temperature falls. A yield of 96 per cent of trichloronitromethane is obtained when the crude product is distilled with steam.

5. Phosgene ($COCl_2$) and Thionyl Chloride ($SOCl_2$) as Chlorinating Agents

Phosgene finds an important use in the preparation of acid chlorides. When vapors of organic acids are mixed with phosgene in the presence of charcoal, these react readily and provide a continuous and comparatively cheap method of preparing acid chlorides. Chloroacetyl chloride is prepared by admitting gaseous phosgene at the rate of 200 liters per hr. and liquid chloroacetic acid at the rate of 900 gm. per hr. into a reaction chamber packed with charcoal and maintained at 200°C. The effluent vapors are led to a reflux condenser, and the chloroacetyl chloride (b.p., 106°C.) passes through, while the chloroacetic acid (b.p., 187°C.) is returned to the reactor. Approximately 900 gm. of chloroacetyl chloride per hour is thus obtained.

Thionyl chloride serves as a useful chlorinating agent for replacing the hydroxyl groups in alcohols and carboxylic acids by chlorine. Compared with phosphorus pentachloride, it has the advantage of forming only volatile reaction products and is consequently preferred for commercial operations.

$$SOCl_2 + HO{\cdot}C_6H_4{\cdot}COOH \rightarrow SO_2 + HCl + HO{\cdot}C_6H_4{\cdot}COCl$$

Thionyl chloride can also be used to convert the higher fatty acids, naphthenic acids as well as aromatic acids, to acid chlorides. Temperatures of 140 to 160° afford a convenient working range. The addition of a tertiary amine which combines with the liberated hydrogen chloride increases the speed of reaction as well as the yield of acid chloride.[1]

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[1] Tindall, U. S. 2,365,981 (1944).

6. Sulfuryl Chloride (SO_2Cl_2) as a Chlorinating Agent

Treatment of Paraffin Hydrocarbons.—Sulfuryl chloride reacts readily with unsaturated paraffins to form the halogen derivatives. It can also be employed to advantage in the chlorination of saturated hydrocarbons, such as methane and ethane.

Previously, it has been shown that the direct chlorination of saturated paraffins is accomplished with considerable difficulty, due to the tendency to explosions, unless special precautions are taken. The advantage of using sulfuryl chloride for chlorinating saturated hydrocarbons resides primarily in the fact that no great amount of heat is evolved when it is used. The dissociation of sulfuryl chloride results in the formation of sulfur dioxide and chlorine, heat being absorbed during the process. The halogen enters into reaction with the hydrocarbon that is present. Approximately two-thirds of the amount of heat evolved by the chlorination of methane or other hydrocarbons is absorbed in effecting the progressive dissociation of sulfuryl chloride. For this reason, it is difficult to cause an explosion when saturated paraffins are mixed with sulfuryl chloride, regardless of the proportions in which the reactants are present.

By regulating the quantity of sulfuryl chloride, it is possible, in the chlorination of methane, to obtain a yield of 50 per cent chloroform.[2] When a lesser quantity of sulfuryl chloride is used, it is obvious that a larger proportion of mono- and dichloromethanes is formed. The reaction is promoted by the presence of ionizing agents such as light, heat, metallic chlorides, and activated carbon. The heat of reaction is slightly greater than the quantity absorbed by the decomposition of sulfuryl chloride. The excess of heat is sufficient to keep the temperature of the hydrocarbon gas at the optimum reaction temperature, without the application of heat after the reaction has started.

The chlorination of methane can be carried out by bubbling the hydrocarbon gas through sulfuryl chloride (b.p., 69°C.) at a predetermined temperature. The higher the temperature the larger the ratio of sulfuryl chloride vapor to hydrocarbon. The mixture of gases is passed through a tube filled with inert material and maintained at about 350°C. The flow is sufficiently rapid to constitute turbulent flow. It is necessary to use only a small quantity of catalyst, *e.g.*, carbon; otherwise, the decomposition of sulfuryl chloride will be too rapid, and the rate of formation of chlorine will then be greater than the reaction between chlorine and methane.

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[1] Graenacher and Rossi, U. S. 2,279,985 (1942).

[2] U. S. 1,765,601 (1930).

Treatment of Aromatic Compounds with SO_2Cl_2.—In the absence of a catalyst, sulfuryl chloride (SO_2Cl_2) does not react readily with such compounds as benzene or halogenated benzene, it being necessary to operate in closed vessels at 150°C. In the presence of aluminum chloride and sulfur or sulfur chloride, chlorination of benzene occurs with vigor at ordinary temperatures. Dichlorobenzene can thus be converted substantially to the tetrachloro derivative.

Sulfuryl chloride can be employed in conjunction with numerous chlorine carriers to effect substitution in either the ring or side chain. The chlorides of antimony, iron, molybdenum, and aluminum are valuable with sulfuryl chloride in effecting substitution in the ring. The chlorides of phosphorus and, to a lesser extent, manganese, arsenic, and bromine favor side-chain substitution. Sulfur accelerates both types of substitution.

Instead of the use of sulfuryl chloride, SO_2 and Cl_2, which combine to give sulfuryl chloride, can be employed for vapor-phase reactions.[1] When the ratio of SO_2 to Cl_2 is adjusted, it is feasible to produce sulfonic or chlorosulfonic acid derivatives of saturated paraffins in liquid-phase reactions. According to Lockwood and Richmond, a premixed stream of sulfur dioxide and chlorine can be used for the countercurrent photochlorination of white oil (petroleum fraction, sp. gr., 0.8033: b.p., 283 to 324°) at about 50°.[2] The product, after hydrolysis with 30 per cent sodium hydroxide, yields an aqueous solution of the sodium salt of a sulfonic or chlorosulfonic acid. An increase in the ratio of SO_2 to Cl_2 greatly increases the yield of solubilized product. When a 3:1 ratio is used, the product contains very little chlorine and has good wetting and detergent characteristics.[3]

Effect of Oxidants.—Kharasch has shown that, in the presence of benzoyl or other organic peroxides, sulfuryl chloride selectively chlorinates the side chain and not the nucleus of alkyl-substituted benzene. The reaction, which is carried out in the dark, is also useful for the chlorination of aliphatic compounds such as acyclic hydrocarbons, cycloparaffins, carboxylic acids, and their acid halides.[4]

The quantity of organic peroxide required is generally about 0.1 per cent based on the SO_2Cl_2 used. The employment of a solvent or diluent such as carbon tetrachloride is advantageous in the chlorination of carboxylic acids that react vigorously and also in the case of solid materials. The data in Table VIII indicate the scope and nature of the results obtained by this procedure.

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[1] Reed, U. S. 2,046,090 (1936).

[2] Lockwood and Richmond, U. S. 2,193,824 (1940).

[3] Fox *et al*, U. S. 2,202,791 (1940).

[4] Kharasch and Brown, U. S. 2,302,228 (1942).

TABLE VIII.—CHLORINATION WITH SULFURYL CHLORIDE IN THE PRESENCE OF BENZOYL PEROXIDE

SO_2Cl_2, moles	Organic reactant	Moles reactant	Reflux hr.	Product yields
0.75	*n*-Heptane	3.0	1	Over-all yield, 85% 15% primary heptyl chloride 85% *sec*-heptyl chlorides
0.2	*n*-Propyl chloride	0.6	4	Over-all yield, 85% 60% 1, 2-dichloropropane 40% 1, 3-dichloropropane
0.2	Toluene	0.4	¼	80% benzyl chloride
0.3	*m*-Xylene	1.0	½	80% *m*-xylyl chloride
0.4	Propionic acid	1.0	1½	Over-all yield, 75% 45% α-chloropropionic acid 55% β-chloropropionic acid
0.6	Cyclohexane	1.8	1½	Over-all yield, 98% 89% chlorocyclohexane 11% dichlorocyclohexane

Acid Chlorides.—Previously, it was shown that thionyl chloride ($SOCl_2$) can be advantageously used for the preparation of acid chlorides from their respective carboxylic acids. Sulfuryl chloride ($SO_2 + Cl_2$) can be similarly employed for the conversion of the alkali metal salts of fatty acids.

$$2R{\cdot}CO{\cdot}ONa + SO_2Cl_2 \rightarrow 2R{\cdot}CO{\cdot}Cl + Na_2SO_4$$

Anhydrides may be formed by condensation during the process, but these may be converted to the desired acid chloride by using an excess of chlorinating agent.

$$\begin{aligned} R{\cdot}CO{\cdot}ONa + Cl{\cdot}OC{\cdot}R &\rightarrow R{\cdot}CO{\cdot}O{\cdot}OC{\cdot}R + NaCl \\ R{\cdot}CO{\cdot}O{\cdot}OC{\cdot}R + SO_2Cl_2 &\rightarrow 2R{\cdot}CO{\cdot}Cl + SO_3 \end{aligned}$$

7. Chlorination with Metal and Nonmetal Chlorides

Ferric Chloride.—In the chapter on the Friedel and Crafts reaction, it is pointed out that aluminum chloride and ferric chloride can exercise a chlorinating action in addition to serving as a condensing agent. Ferric chloride is particularly valuable in the preparation of alkyl chlorides from their respective alcohols. The metal halide serves, therefore, as an esterification agent; but in such reactions it functions best in the presence of hydrochloric acid.

Chlorination with Antimony Pentachloride.—In addition to serving as a halogen carrier for direct chlorinations, antimony pentachloride itself can be employed as a chlorinating agent. The addition of chlorine to acetylene can be effected by introducing acetylene into the liquid antimony halide and then decomposing the addition compound that is formed. Saturated gaseous paraffins can be chlorinated similarly by passing the hydrocarbon vapors through a column at 300°C. filled with quartz impregnated with cuprous chloride and over which liquid antimony pentachloride is permitted to flow. The antimony trichloride recovered from the operation is treated with chlorine gas to regenerate the pentahalide. The chlorinated products of methane comprise CH_3Cl, CH_2Cl_2, and $CHCl_3$, the monochloro derivative predominating.

When the chlorination is carried out below 100°C., saturated paraffins are practically unaffected by antimony pentachloride. It is thus feasible and economical to treat unsaturated hydrocarbons of the ethylene series containing saturated hydrocarbons as impurities.[1] The reactions may be represented by the following equation:

$$C_nH_{2n} + SbCl_5 \rightarrow C_nH_{2n}Cl_2 + SbCl_3$$

The reactions proceed rapidly and completely, with the production exclusively of dichloro addition compounds, no chlorination taking place by substitution.

Phosphorus Chlorides as Chlorinating Agents.—At moderate temperatures, PCl_5 is almost as powerful a chlorinating agent as chlorine; and at higher temperatures its behavior is approximately of the same order. The liberation of chlorine from PCl_5 takes place according to the law of mass action, as can be seen from a consideration of the following system, all the components

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \frac{(PCl_3)\cdot(Cl_2)}{(PCl_5)} = K$$

being in the vapor phase. The formation of PCl_5 is favored by the application of pressure, whereby PCl_3 and Cl_2 combine; the liberation of chlorine is favored by an increase in temperature and an opportunity for the free movement of the vapors. The dissociation of PCl_5 at various temperatures is as follows:

Temperature, °C.	182	200	250	300
Percentage decomposition	41.7	48.5	80	97.3

Phosphorus pentachloride is employed as an esterification agent in the treatment of alcohols, the halide becoming hydrolyzed during the reaction:

Acid Chlorides.—Acid chlorides can be made from the corresponding fatty acids by treatment with phosphorus halides. When liquid carboxylic acids are reacted, the phosphorus halide, PCl_3 or $POCl_3$, may be added gradually. If the acid does not react energetically, as in the case of the higher members of the acetic acid series or with aromatic acids, phosphorus pentachloride is used. The reactions may be represented as follows:

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[1] U. S. 1,754,656 (1930).

$$R{\cdot}COOH + PCl_5 \rightarrow R{\cdot}COCl + POCl_3 + HCl \qquad (1)$$
$$3R{\cdot}COOH + 2PCl_3 \rightarrow 3R{\cdot}COCl + P_2O_3 + 3HCl \qquad (2)$$
$$2R{\cdot}COONa + POCl_3 \rightarrow 2R{\cdot}COCl + NaPO_3 - NaCl \qquad (3)$$

Phosphorus oxychloride is used ordinarily when treating salts of the carboxylic acids. This reaction [(Eq. (3)] may be used to advantage in order to utilize more of the chlorine of PCl_5 than is the case when the latter acts upon the free acids. When the pentachloride reacts with the sodium salt, as above, $POCl_3$ is formed as an intermediate compound; and although this no longer has the capacity to act on free fatty acid, it can convert two other molecules of the salt into the acid chloride:

$$3CH_3COONa + PCl_5 \rightarrow 3CH_3COCl + NaPO_3 + 2NaCl$$

When acetyl chloride is desired, it can be readily made according to Eq. (2) above by adding phosphorus trichloride to boiling acetic acid. The acetyl chloride (b.p., 55°) is condensed while the hydrogen chloride is led to an absorption system.

Phosphorus trichloride is also used to convert stearic, lauric, and other higher fatty acids to the corresponding acid chlorides. An excess of PCl_3 must be used, and this is removed by washing the upper layer of the settled charge with water.[1]

8. Halogenation by the Sandmeyer Reaction

Replacement of Diazonium Group.

$$C_6H_5{\cdot}N_2{\cdot}Cl + Cu_2Cl_2 \xrightarrow{HCl} C_6H_5{\cdot}Cl + N_2 + Cu_2Cl_2 \qquad (a)$$
$$2C_6H_5{\cdot}N_2{\cdot}Cl + Cu_2Br_2 \xrightarrow{HBr} 2C_6H_5{\cdot}Br + 2N_2 + Cu_2Cl_2 \qquad (b)$$
$$C_6H_5{\cdot}N_2{\cdot}SO_4H + KI \xrightarrow{HI} C_6H_5I + N_2 + KHSO_4 \qquad (c)$$

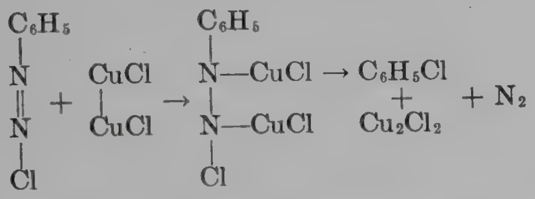
The Sandmeyer reaction is a valuable procedure for the preparation of halogen derivatives that generally cannot be made by other more direct methods. When diazonium salts, which are unstable and unsaturated bodies, react with halogen hydracids alone or, preferably, in the presence of the corresponding cuprous salt, nuclear halogen derivatives are formed, and nitrogen is evolved. Although this procedure is comparatively costly, it makes possible obtaining specific halogenated derivatives in a high state of purity. In a number of syntheses, the Sandmeyer reaction is used in conjunction with other methods of halogenation to secure polyhalogenated derivatives.

The reaction involves the preparation of a solution of the diazonium halide and gradually adding it to a solution of the corresponding cuprous

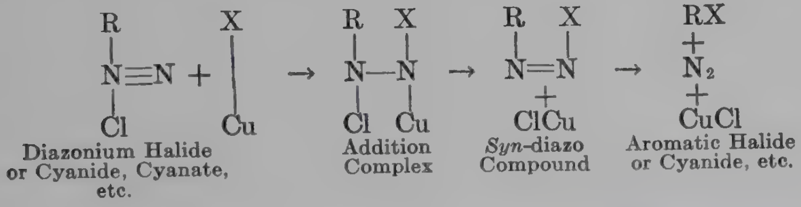
[1] U. S. 2,262,431 (1941).

halide. In the preparation of compounds that are volatile, it is essential to employ a reflux condenser. In some cases, the diazo solution is prepared in the presence of the cuprous halide. Under such circumstances, a solution of sodium nitrite is added to a heated acid solution of the amine and copper salt. The diazotization and replacement of the diazo group then takes place in one operation.

The reaction scheme for the conversion of benzenediazonium chloride to chlorobenzene, as formulated by Sandmeyer, is as follows:



A more general formulation based on the known formation of colored intermediate addition compounds, which takes into consideration the preparation of other halides, the nitrile, and other derivatives, has been proposed.[1]



In the Gattermann reaction, the identical processes are carried out in the presence of pure, finely divided copper. For the preparation of nitriles, however, the Sandmeyer reaction gives uniformly better results.

Copper is not the only metal that can advantageously be employed for the replacement of the diazo group by halogen. When the precaution is taken to ensure a maximum concentration of chloride ions, saturated solutions of calcium chloride, zinc chloride, and zinc-ammonio chloride often give equally good results.

Eichenberger holds two factors of decisive importance in considering the dynamics of the Sandmeyer reaction: (*a*) the activation energy required to discharge the chloride ions; and (*b*) the operation of the law of mass action.[2] It is evident that in solutions containing hydroxyl as well as halogen ions, the former will move with a greater velocity and react more readily and therefore play a prominent role in the formation of phenols. But, on the other hand, from the law of mass action, it would be expected that in a solution containing different ions, each will react in proportion to its concentration. From the consideration of molecular or ionic concentration alone, practically theoretical yields of aryl halide would be expected when maximum concentrations of HCl and $ZnCl_2$ are used in the Sandmeyer reaction.

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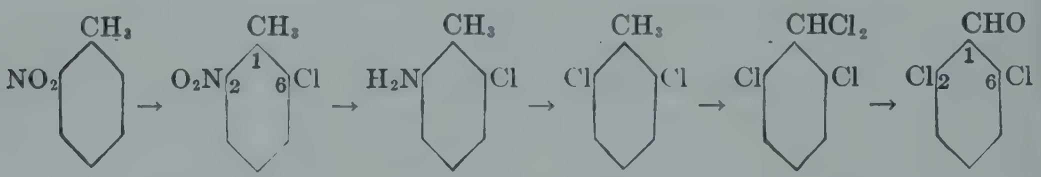
[1] Hantzsch, *Ber.*, **27**, 1702 (1894); Eichenberger, Dissertation E. T. H., Zurich, 1929.

[2] Eichenberger, Dissertation E. T. H., Zurich, 1929.

The mechanism of the Sandmeyer reaction may consequently be explained as follows: The aryldiazonium compound first forms an addition compound with cuprous salts, resulting in a complex cation which subsequently undergoes decomposition. In this process, it is not the halogen inherent in the diazonium compound or the free halogen ions of the reaction solution but the halogen of the copper halide by virtue of its closer proximity to the aryl radical that enters the nucleus. That quantitative yields are never obtained in carrying out this reaction is explicable on the hypothesis that the diazonium salt reacts with OH^- ions before the addition complex is formed.

Progressive Halogenation by Different Methods.—In some syntheses, it is necessary to employ two or more methods of halogenation in order to obtain the desired halogen compound. An interesting example is the preparation of 2, 6-dichlorobenzaldehyde from *o*-nitrotoluene. The reactions involved are shown in the following graphic representation:



I
Direct nuclear chlorination

II

III
Chlorination, Sandmeyer reaction

IV
Side-chain photo-chlorination

V

1. The nuclear chlorination of toluene is carried out with gaseous chlorine at 20 to 40°C., using steel turnings as catalyst.

2. The reduction of the nitro group is accomplished by the usual iron-acid method. The reduction charge is made alkaline with soda ash, and the 6-chloro-*o*-toluidine is distilled with steam.

3. The amino group is replaced by chlorine through the Sandmeyer reaction, and 2, 6-dichlorotoluene is thus obtained. The diazonium solution, which is prepared separately, is delivered slowly to the copper chloride solution at 70 to 80°C. The dichlorotoluene is distilled with steam and then purified by washing with caustic soda solutions and distilling *in vacuo*.

4. The side-chain chlorination of 2, 6-dichlorotoluene to form 2, 6-dichlorobenzal chloride is carried out in glass apparatus provided with a reflux condenser. Mercury quartz lamps are used to catalyze the chlorination, chlorine gas being admitted until the increase in weight corresponds to the formation of the benzal chloride derivative. The

product is distilled *in vacuo*, since higher chlorinated products and resins are formed.

5. The hydrolysis of 2, 6-dichlorobenzal chloride is accomplished with 93 per cent sulfuric acid by heating at 50 to 60°C. The reaction mass is diluted, and the corresponding benzaldehyde distilled with steam.

BROMINATION

In general, methods similar to chlorination with chlorine and chlorides can be employed in the preparation of bromine derivatives. Because the reaction is milder, the bromination of the paraffin hydrocarbons does not, however, proceed so rapidly or to so great a degree; and with the lower permissible operating temperature, the formation of polybromine compounds occurs to a lesser extent.

In brominations, it is generally advisable to employ a compatible solvent, not only for the organic compound but also for the bromine. Water, dilute alkali, glacial acetic acid, concentrated sulfuric acid, methanol, chloroform, carbon disulfide, and carbon tetrachloride can thus be employed. The use of such cosolvents serves to ameliorate the reaction and thus subjects it to closer control.

The choice of the solvent will, of course, depend on the reactants employed and their specific reactivity in various solvents. Thus, benzaldehyde takes up bromine in carbon tetrachloride about a thousand times as rapidly as it does in chloroform or carbon disulfide.[1] The bromination leads to the formation of bromobenzyl benzoate according to the following reactions:

$$C_6H_5{\cdot}CHO + Br_2 \rightarrow C_6H_5{\cdot}COBr + HBr \qquad (I)$$
$$C_6H_5{\cdot}COBr + C_6H_5{\cdot}CHO \rightarrow C_6H_5{\cdot}COO{\cdot}CHBr{\cdot}C_6H_5 \qquad (II)$$

The reactivity of aromatic side-chain compounds toward brominating agents is also influenced by the nature of the solvent. Under comparable conditions, the percentage formation of benzyl bromide from bromine and toluene in various solvents is as follows:[2]

$CS_2 = 85.2$; $CCl_4 = 56.6$; $CH_3COOH = 4.0$; $C_6H_5NO_2 = 2.0$.

This same influence is exhibited not only in the dark, but also in photobrominations. From the preceding data, Bruner has concluded that solvents such as nitrobenzene and acetic acid, which have strong ionizing (dissociating) powers, favor substitution in the nucleus.

Addition Reactions with Bromine.—Bromine in aqueous solution forms addition compounds readily with unsaturated organic compounds. This reaction is of considerable interest, since it provides an analytical method for the detection and estimation of double bonds.

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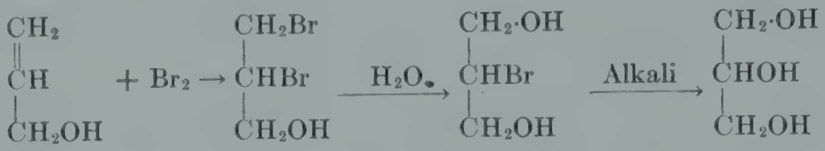
[1] HERZ and DICK, *Ber.*, **41**, 2645 (1908).

[2] BRUNER and VORBRODT, *Chem. Zentr.*, **33**, 557 (1909).

Allyl alcohol on bromination takes on two atoms of bromine, one of which is hydrolyzed when the reaction is carried out in aqueous solutions. In the presence of an excess of alkali, the second bromine is split off with the formation of glycerol.[1]



$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} + Br_2 \rightarrow \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2{\cdot}OH \\ | \\ CHBr \\ | \\ CH_2OH \end{array} \xrightarrow{\text{Alkali}} \begin{array}{l} CH_2{\cdot}OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Addition of HBr.—Kharasch and coworkers have shown that the addition of HBr to the double bonds of olefinic hydrocarbons or substituted olefinic hydrocarbons is influenced by the presence of either peroxides or antioxidants. Normal additions occur in the absence of peroxides; and in practice this condition can be brought about by working under carefully controlled conditions or by the addition of antioxidants to the reaction mixture. Among the antioxidants found to be effective are diphenylamine, thiophenol, and thiocresol, the first being the least effective of the three. Benzoyl peroxide and ascaridole (Δ-2, *p*-menthene-1, 4-dioxide) are useful in ensuring a peroxide-catalyzed addition of HBr and HI to olefins.

In Table IX are presented typical data illustrating the influence of peroxides and antioxidants.

TABLE IX.—INFLUENCE OF PEROXIDES AND ANTIOXIDANTS

Compound treated	Addition agent	Normal product	Addition agent	Catalyzed product
$CH_2{=}CHBr$	Diphenylamine	$CH_3{\cdot}CHBr_2$	Air	$CH_2Br{\cdot}CH_2Br$
$CH_3CH{=}CH_2$	Thiocresol	$CH_3CHBrCH_3$	Benzoyl peroxide	$CH_3CH_2CH_2Br$
$CH_3CH_2CH{=}CH_2$	None	$CH_3CH_2CHBrCH_3$	Ascaridole	$CH_3CH_2CH_2CH_2Br$
$CH_3{-}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{=}CH_2$	Diphenylamine	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}BrCH_3$	Ascaridole	$CH_3{\cdot}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}{\cdot}CH_2Br$
$CH_3(CH_2)_{10}CH{=}CH_2$	Antioxidant	2-Bromotridecane	Peroxide	1-Bromotridecane

It is clear from the above data that the addition of HBr to the alkenes containing terminal double bonds results in the formation of primary bromides whenever "peroxides" are present in the reaction mixture. Secondary and tertiary bromides are formed during the normal addition in the presence of "antioxidants" in accordance with Markownikow's rule. In general, the yields of the alkyl halides are high and the formation of the specific product is almost quantitative.

Some olefins, *e.g.*, vinyl bromide and allyl bromide, are very sensitive to peroxides; whereas others, *e.g.*, butene-1, are comparatively insensitive. Kharasch has found that external conditions such as solvents, light, and temperature have a very powerful effect on those systems which are sensitive to peroxides but practically no effect on those which are comparatively insensitive. Peroxides are the most important single factor governing the direction of addition; and, in all probability, this is due to their action on the hydrogen bromide or the unsaturated compound or both *before* addition actually takes place. The physical and chemical agencies such as light, solvent, and temperature, exert their peculiar influence on the peroxide molecules or in activating the oxygen liberated by the decomposition of the peroxides.

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[1] STRITAR, *Chem. Ztg.*, **43**, 23 (1919).

IODINATION

Although chlorine and bromine react with methane and other saturated hydrocarbons, iodine enters into combination only under exceptional circumstances. Chlorine and bromine react with hydrogen with the evolution of heat, whereas under the same conditions (400°C.) hydrogen iodide is formed with the absorption of heat. Since the heat of formation is a measure of the strength of the bond, then, compared with the halogens of lower molecular weight, iodine exhibits a stronger tendency to combine only loosely and to enter into reversible reactions.

Treatment of Aliphatic Compounds. *Addition.*—Iodine and hydriodic acid combine readily with unsaturated paraffin hydrocarbons. When ethylene gas is passed into a warm solution of iodine in alcohol, the two substances unite:

$$H_2C{:}CH_2 + I_2 \rightarrow IH_2C{\cdot}CH_2I \text{ Ethylene Diiodide}$$

With hydriodic acid, the reaction takes place with the formation of ethyl iodide.

Replacement.—1. Chlorine and bromine may be replaced by iodine in many compounds by heating the derivative with an alkali iodide:

$$CH_3{\cdot}CH_2Cl + KI \rightarrow CH_3{\cdot}CH_2I + KCl$$

2. Alkyl iodides may be prepared (*a*) by the reaction of PI_3 with an alcohol. In practice, this is generally accomplished by digesting red phosphorus with an anhydrous alcohol and then adding iodine. The mixture is heated under a reflux condenser and finally distilled:

$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + P(OH)_3$$

(*b*) By treating an alcohol with hydriodic acid, the reaction taking place according to the following equation:

$$CH_3OH + HI \rightarrow CH_3I + H_2O$$

The process may be made continuous, by adding the alcohol gradually and keeping the temperature sufficiently high so that the water distills over as it is formed. Methyl iodide is prepared by heating methyl alcohol with sodium iodide and sulfuric acid.

3. The action of iodine on either acetone or alcohol, in a mildly alkaline solution, will yield iodoform

$$C_2H_5OH + 8I + 6KOH \rightarrow CHI_3 + HCOOK + 5KI + 5H_2O$$

Industrially, iodoform is prepared by electrolysis, at 60 to 65°C., of a solution of 60 kg. of KI, 20 kg. of Na_2CO_3, and 80 liters of ethanol per 400 liters of solution. The iodine set free by the current converts the ethanol and the sodium carbonate into iodoform and sodium iodide. In practice, part of the iodine reacts with the caustic alkali formed at the cathode and forms an iodate. Prevention of this reaction by surrounding the cathode with a porous cup brings the yield of iodoform up to about 90 per cent of the theoretical.

Aromatic Compounds. *Substitution.*—Direct substitution of iodine into the benzene nucleus is feasible only in the presence of an oxidizing agent. The hydrogen iodide formed simultaneously with the iodo compound is unstable: the iodine in the benzene nucleus is loosely bound; and conditions must therefore be provided to avoid reversibility.

$$2C_6H_6 + I_2 + (O) \rightarrow 2C_6H_5I + H_2O$$

1. Benzene treated in a sealed tube with iodine and iodic acid under suitable conditions will yield iodobenzene. The iodic acid oxidizes the hydrogen iodide as it is formed, thus preventing the reduction of the iodobenzene to benzene.

2. The method of Varma and Panickar, which involves the use of sodium nitrite and fuming sulfuric acid, may be employed for the iodination of aromatic compounds.[1] Nitric acid can be used advantageously as the oxidant for the liberated hydriodic acid.[2] The procedure as applied to the production of iodobenzene involves the reaction of 1.5 moles of iodine with 5.1 moles of benzene in the presence of 6.15 moles of nitric acid.[3] The yield is in excess of 85 per cent of the theoretical. Other benzenoid compounds are iodinated in a similar manner. It should be noted that in this reaction, all the halogen enters into the benzene compound, unlike ordinary direct halogenations in which half of the halogen used is given off as halogen hydride.

3. Phenols may be iodinated by treatment with iodine in the presence of strong ammonia. 2, 4, 6-Triiodophenol is prepared quantitatively by treatment of phenol in concentrated aqueous ammonia with iodine

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[1] Varma and Panickar, *Quart. J. Indian Chem. Soc.*, **3**, 342 (1926).

[2] Datta and Chatterjee, *J. Am. Chem. Soc.*, **39**, 437 (1917).

[3] Dains and Brewster, "Organic Synthesis," Collective Vol. I, p. 316, John Wiley & Sons, Inc., New York, 1932.

until the color of iodine persists. Phenolic compounds, in general, are susceptible to the foregoing method.

FLUORINATION

Under atmospheric conditions, fluorine attacks with violence all organic compounds; ether, benzene, and turpentine take fire immediately on contact with it. The fluorine derivatives of organic compounds are consequently made by indirect methods from materials that have been rigorously dried. Of the nine indirect methods shown on page 172 for the preparation of fluorine derivatives, the displacement process is undoubtedly the one most widely used. Whereas the direct fluorination of hydrocarbons proceeds with such vigor as to cause carbonization, the replacement of Cl by F in polyhalogenated compounds can be accomplished smoothly by the use of fluorides at ordinary temperatures. Hydrofluoric acid, antimony trifluoride, and boron trifluoride are the fluorinating agents most frequently employed. A catalyst is necessary, and ordinarily iodine, bromine, or a metal pentachloride is used.

When fluorine gas is led into a flask containing carbon tetrachloride, practically no fluorination takes place up to 40 to 50°C. At 77°C., the boiling point of CCl_4, the introduction of fluorine results in an explosive reaction.[1] If, in a similar reaction, 5 per cent by weight of iodine is added to the charge, the introduction of fluorine results in the formation of a flame at the tip of the fluorine inlet, and the presence of iodine chlorides is observed in the vapors leaving the reaction chamber. Analysis of the condensed reaction products shows the presence of all four stages of fluorinated methane—CCl_3F to CF_4.

In general, it may be stated that fluorides of the less positive metals, *e.g.*, Ag, Hg, and Sb, are useful in replacing other halogens by fluorine.[2] Thus, Swarts found that antimony trifluoride in the presence of bromine could be used for the fluorination of a large number of organic compounds.[3] Chlorides may also be employed instead of bromine to catalyze such fluorinations.

The reaction involved in the manufacture of dichlorodifluoromethane, which is used widely as a refrigerant, is as follows:

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

Since the introduction of each atom of fluorine lowers the boiling point of the resulting compound by about 52°C. (Fig. 9), it is a relatively simple matter to extract any desired substitution product by fractional distillation.[1] By regulation of the temperature of the dephlegmating column, which is an integral part of the reaction system, the desired product is removed as it is formed. Small amounts of excessively or insufficiently fluorinated compounds will accompany the principal product, but yields of 88 to 94 per cent of dichlorodifluoromethane are obtained directly.

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[1] RUFF and KEIM, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).

[2] SWARTS, *Bull. Soc. Chem.*, **35**, 1533 (1924).

[3] *Ibid.*

The reaction may be carried out at atmospheric pressure; but if dichlorodifluoromethane is the desired product, a large amount of refrigeration will be necessary for dephlegmation. Therefore, it is more economical to run at 60 lb. pressure and to use water to maintain the dephlegmator at 15°C. The technical application of this reaction may be carried out as a batch operation or in a continuous manner.[2]

Treatment of Diazonium Compounds with Borofluorides.—When aryldiazonium sulfates are treated with a large excess of hydrofluoric acid, the corresponding aryl fluorides are obtained. A better and more practical method involves the use of borofluoric acid HBF_4 or its sodium salt. Aryldiazonium chlorides are readily converted by means of sodium borofluoride to the aryldiazonium borofluorides, and these compounds are converted to aryl fluorides by thermal decomposition. The following equations, in which aniline is used as a typical amine, may be employed to represent the several reactions involved:

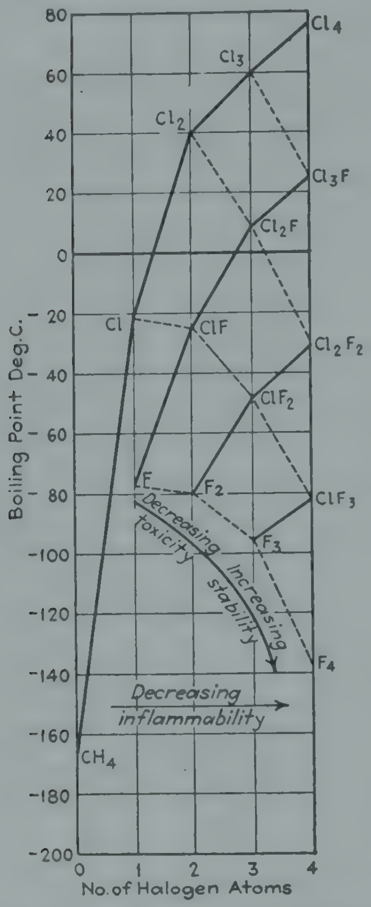

FIG. 9.—Properties of chlorofluoromethanes.

$$C_6H_5NH_2{\cdot}HCl + NaNO_2 + HCl \rightarrow C_6H_5N_2Cl + NaCl + H_2O \qquad (1)$$

$$C_6H_5N_2Cl + NaBF_4 \rightarrow C_6H_5N_2BF_4 + NaCl \qquad (2)$$

$$C_6H_5N_2BF_4 \rightarrow C_6H_5F + BF_3 + N_2 \qquad (3)$$

The control of the hydrogen-ion concentration during the formation of the aryldiazonium borofluoride is an important matter; for when this is excessive, the yields are not so satisfactory. For this reason, sodium borofluoride is used in part at least to precipitate the diazonium borofluoride. When borofluoric acid is used as the precipitant, the free acid formed by double decomposition builds up during the reaction and exerts a deleterious effect.[1]

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[1] MIDGLEY and HENNE, *Ind. Eng. Chem.*, **22**, 542 (1930).

[2] Fr. 720,474 (1932); 701,324 (1931); Ger. 552,919 (1932).

IV. CHLORINATION IN THE PRESENCE OF A CATALYST

The catalytic agents most frequently employed in chlorinations are metallic iron, cupric oxide, bromine, iodine, sulfur, the halides of iron, antimony, tin, arsenic, phosphorus, aluminum and copper, and vegetable and aminal carbons.

Although the halogen carriers exert a powerful influence in promoting ring substitution in the chlorination of aromatic side-chain compounds and also markedly affect the ratio of disubstituted isomers,[2] they have no considerable effect upon the relative reaction rates of primary and secondary hydrogen atoms in paraffin molecules.[3]

Iron Salts as Catalysts.—The preparation of chlorobenzene is the classic example of chlorination in the presence of iron. Of considerable interest also is the chlorination of nitrobenzenes, since this leads to meta derivatives, whereas the nitration of the chloro derivatives leads to para and ortho compounds.

The preparation of carbon tetrachloride from carbon disulfide is also frequently brought about through the catalytic intervention of iron. The operation is carried out in two steps:

$$CS_2 + 3Cl_2 \xrightarrow{Fe} S_2Cl_2 + CCl_4 \qquad (1)$$

The products are separated by distillation, and the sulfur chloride is subsequently reacted with fresh carbon disulfide.

$$CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S \qquad (2)$$

On cooling, most of the sulfur is precipitated and the supernatant liquid is drawn off and fractionated. The recovered sulfur is reconverted to carbon disulfide.

Antimony pentachloride is an excellent chlorine carrier. It has been used extensively for the manufacture of tetrachloroethane, ethylene dichloride, tetrachlorophthalic anhydride, and aliphatic hydrocarbons in general; and when it is used for the manufacture of tetrachloroethane $Cl_2HC \cdot CHCl_2$ from acetylene,[4] an equimolecular double compound of acetylene and antimony pentachloride is formed, which may be chlorinated without danger of explosive reactions:

$$2Cl_2 + SbCl_5 \cdot C_2H_2 \rightarrow C_2H_2Cl_4 + SbCl_5$$

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[1] U. S. 1,916,327 (1933).

[2] Stoesser and Smith, U. S. 1,946,040 (1934).

[3] Hass, McBee, and Hatch, *Ind. Eng. Chem.*, **29**, 1337 (1937).

[4] Ger. 154,657 (1903); Fr. 346,652 (1903).

To ensure a smooth reaction, a mixture of tetrachloroethane and antimony trichloride is first placed in the chlorinating vessel, and the chlorine and acetylene are delivered into the charge through separate lines T_1T_2 (Fig. 10). The gases and liquid are brought into intimate contact by means of an efficient agitator and circulated through the gates *L*. The reaction mass is kept cool by cold water circulating through lead coils.

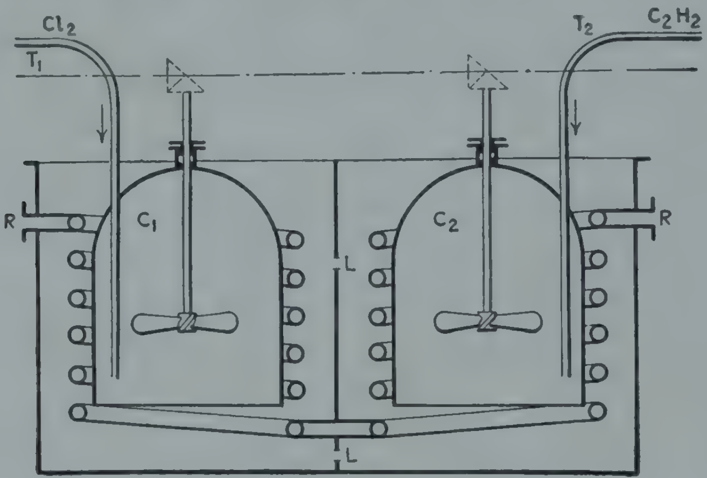


FIG. 10.—Apparatus for chlorination of acetylene.

Bromine and iodine, because of their capacity to form mixed halogens, *e.g.*, BrCl and ICl which have a low energy of activation, are excellent chlorinating catalysts. In general, it can be stated that small quantities of iodine and bromine are frequently added along with other less costly chlorine carriers, and the literature records numerous examples of such halogenations.

Sulfur and sulfur chloride (S_2Cl_2) are important and efficacious catalysts. They are used for the conversion of glacial acetic acid into monochloroacetic acid, the latter compound being employed for the synthesis of ω-chloroacetophenone (tear gas) and indigo. It is necessary to carry out this chlorination at the boiling point of glacial acetic acid; for in the cold, acetyl chloride is obtained.

In the presence of sulfur or antimony pentasulfide, CS_2 is transformed into CCl_4. This reaction may be carried out simply by bubbling chlorine gas through boiling carbon disulfide containing free sulfur.

Valence and Catalytic Activity.—The catalytic activity of metal halides or mixed halogens that can exist in two valences in chlorination is probably comparable to the activity of some of such compounds in oxidation processes. Thus, it is known that HOCl, which forms an addition compound by adding on at an ethylenic linkage, can enter into reactions involving either oxidation or chlorination. The factors that determine the course of the subsequent rearrangement and dissociation are principally (1) the concentration of the reactants; (2) the nature of the material undergoing treatment; and (3) the temperature of the reaction.

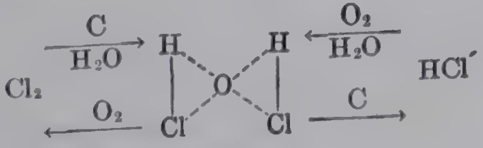
The reactivity of HOCl is related to the analogous activity of the compounds, which occur as unstable intermediate compounds in organic synthesis. Thus, HOCl is a stronger oxidizing agent than $HClO_3$, although the latter contains more oxygen. This behavior is quite a general phenomenon.[1] When compounds intermediate in state of oxidation decompose spontaneously into higher and lower state, they are more powerful oxidizing agents than the higher compound and more powerful reducing agents than the lower one.

Chlorinations Catalyzed by Porous Carbons.—When organic compounds, *e.g.*, the vapors of saturated hydrocarbons, are introduced into a system containing chlorine and a porous carbon, a reaction occurs that leads to the formation of hydrogen chloride and a chlorine derivative of the organic compound. The activity of coke, graphite, and activated carbons depends essentially on their contact surface and appears to be due in part to the influence of capillary forces on the reaction velocities.

In the presence of porous substances such as charcoal, gases or vapors are condensed as a result of capillary forces and pass by adsorption into the liquid state. When two gases capable of slow reaction are brought into contact with a porous carbon, if adsorption occurs, this will increase their concentrations and augment the rate of reaction accordingly.

When gases or vapors are adsorbed at atmospheric pressure in porous carbons, it is found that they occupy only a fraction of their original volume, and it is presumed that some of the vapors must have been compressed into the liquid state. It may be supposed, therefore, that, in such porous bodies, layers of adherent molecules are strongly compressed, as a result of which local increases in concentration, pressure, and temperature occur. Such conditions are favorable to the formation of active molecules and to their encounter with one another. Whether or not these collisions lead to the preliminary formation of addition compounds that undergo dissociation cannot be definitely stated, although this appears probable.

It is known that, in the presence of carbon and moisture, molecular chlorine is readily transformed into hydrochloric acid and that, in the presence of oxidants, chlorine is liberated from hydrochloric acid. Presumably, a common active intermediate compound is formed in such oxidation-reduction reactions—because both methods are useful in carrying out chlorinations.



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[1] Luther, *Z. physik. Chem.*, **36**, 385 (1901).

V. PHOTOCATALYTIC CHLORINATIONS

The influence that light can exert on the progress of a chlorination is of great technical importance, especially when this influence is selective. Whereas nuclear hydrogen is not affected by light, the substitution of side-chain hydrogen by chlorine is strongly influenced, and this phenomenon is utilized industrially for the preparation of side-chain halides from toluene.

The effects of photocatalysis depend on two quite distinct factors, the quantity of light present and the quality of this light, factors directly influenced by the absorption of the medium. This absorption is evidently not the same for all radiations. The intensity of any radiation decreases geometrically as the thickness of the absorbent layer increases arithmetically. Thus, with a layer x mm. thick, the intensity of a radiation i, after penetration of the surface, is I/n^x, where I is the initial intensity and n is a factor dependent both on the medium and on the original radiation, for the rapidity with which a radiation is absorbed by any medium depends upon the nature of the radiation. For solids, n is generally of considerable magnitude; it decreases greatly in the case of liquids and becomes very small in the case of gases. If the thickness traversed be very great, the intensity of the radiation may be reduced practically to zero.

The excitation produced by light on chlorination reactions is sometimes so violent that the reaction becomes explosive, as in the classical example of hydrogen and chlorine. Similarly, chlorine gas saturated with vapors of methyl formate in the darkness can be kept in a stoppered flask for some time in a black box; but when the flask is brought out into the light, a violent detonation ensues. This remarkable phenomenon takes place in any sort of weather, even in the total absence of ultraviolet rays.

The violence of certain exothermic chlorinations may be explained by the facility of the medium to transmit with extreme rapidity the heat evolved when the equilibrium is disturbed by luminous excitation. This phenomenon occurs only in the case of gases. The gaseous state is, in fact, the only one capable of aiding the explosion phenomenon, because of the very high velocity of the molecules in the gas and the great numbers of collisions per second between these molecules, a number that increases with pressure.

In contrast to the photochlorination of toluene and its homologues, Hass has found that in the chlorination of paraffins the ratios of the isomeric compounds are unaffected by the presence or absence of light.[1] Light, however, causes an accelerated reaction rate at lower temperatures showing that most of the chlorination is caused by the absorption of photons. These results would seem to indicate that the reaction mechanism is the same whether the chains are initiated by some catalytic effect at the carbon surfaces, inside the reactor, by the reaction

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[1] HASS, MCBEE, and WEBER, *Ind. Eng. Chem.*, **28**, 335 (1936).

$$Cl_2 + h\nu \rightarrow 2Cl$$

or by the simple thermal dissociation of chlorine molecules.[1]

A reaction mechanism that is consistent with the available data is the following.[2]

$$\begin{gathered} Cl_2 \rightarrow 2Cl \\ R{\cdot}H + Cl \rightarrow R— + HCl \\ R + Cl_2 \rightarrow RCl + Cl \end{gathered}$$

In thermal chlorination, the chlorine atoms are produced by some wall reaction; whereas in photochemical chlorination the chlorine molecules are decomposed by absorbing a quantum of blue light, and the reaction chains are thus initiated.

VI. DESIGN AND CONSTRUCTION OF EQUIPMENT FOR HALOGENATION

From the preceding survey of halogenations, it is obvious that no general rules can be formulated for the design and construction of the plant. Conditions vary so greatly, not only as regards continuous or batch operations but also with the chemical and physical characteristics of the organic compound undergoing treatment. Reactions in the vapor phase, particularly those accelerated by light (Fig. 11), require equipment that differs markedly from that which is suitable for the liquid-phase chlorination of naphthalene or anthraquinone derivatives.

The materials of construction are, however, limited, because of the inability of most products to withstand the corrosive action of hydrogen chloride or hydrochloric acid. With nonaqueous media, apparatus constructed of iron, iron or other alloys, copper or autogenously welded lead is the most suitable, though chemical stoneware, fused quartz, glass, or glass-lined equipment can be used for either the whole plant or specific apparatus. In aqueous media when hydrochloric acid is present in either the liquid or vapor phase and particularly when under pressure, tantalum is undoubtedly the most resistant material of construction. Reactors and catalytic tubes lined with this metal give satisfactory service for prolonged periods.

Resinous woods, in particular red or pitch pine, are satisfactory materials for constructing reaction vats. All hoops and tie rods should be covered with lead or else coated with a mixture of tar and silicates (prodorite) or tar and pitch, to diminish corrosion and dislocation.

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[1] Coehn and Wassiljewa, *Ber.* **42,** 3183 (1909).

[2] Pease and Walz, *J. Am. Chem. Soc.*, **53,** 3728 (1931).

Large apparatus of enameled cast iron is not suitable for chlorinations in which the hydrochloric acid is not immediately absorbed or removed. Experience with such apparatus has given evidence that the enamel may be attacked at a weak point of such a large surface. Once the enamel has been completely penetrated at any point, a rapid attack on the whole vessel follows.

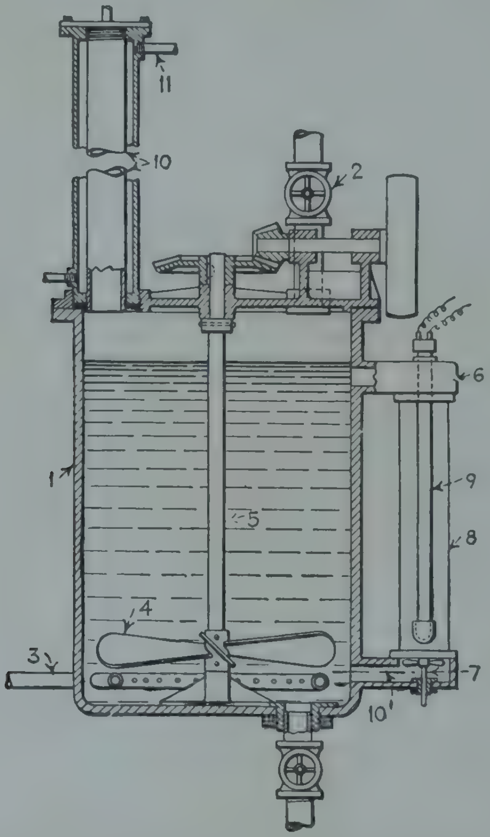


FIG. 11.—Apparatus for photochlorinations.

1. Vessel for chlorinated hydrocarbon.
2. Inlet for hydrocarbon.
3. Inlet for chlorine.
4, 5. Shaft and propeller.
6, 7. Circulating tunnels.
8. Glass reaction vessel.
9. Mercury vapor lamp.
10. Reflux condenser.
11. Vent for hydrogen chloride.

When a chlorination has to be carried out at a low temperature, it is more convenient and economical to circulate the cooling water through a lead coil within the chlorinator or circulate the charge through an outside cooling system rather than to make use of an external jacket. When the temperature is to be maintained at 0°C. or below, a calcium chloride brine, cooled by a refrigerating machine, is employed. When the chlorination necessitates the use of light, flanged joints on the lid, closed by glass 8 to 12 mm. thick, permit satisfactory illumination under gastight conditions.

Chlorinators should be provided with sight glasses to permit observations on the progress of the reaction. These observation tubes are interposed in the gas-exit pipe and are illuminated by an electric lamp. The longer the tube the more delicate are the observations made with it, and the escape of very small amounts of chlorine can be detected by the color of the gas.

When inert diluent gases are employed in the chlorination of hydrocarbons, a plant similar to that snown in Fig. 12 may be used.[1] Here part of the liberated hydrogen chloride resulting from the chlorinating operation is recirculated and fortified with chlorine gas. This gaseous mixture and a gaseous hydrocarbon, such as methane, are led into the reactor 1, and the products of chlorination separated by cooling. The residual gases, containing hydrogen chloride and hydrocarbon mist, may be preheated by passing through heat exchangers, thus utilizing the heat of reaction.

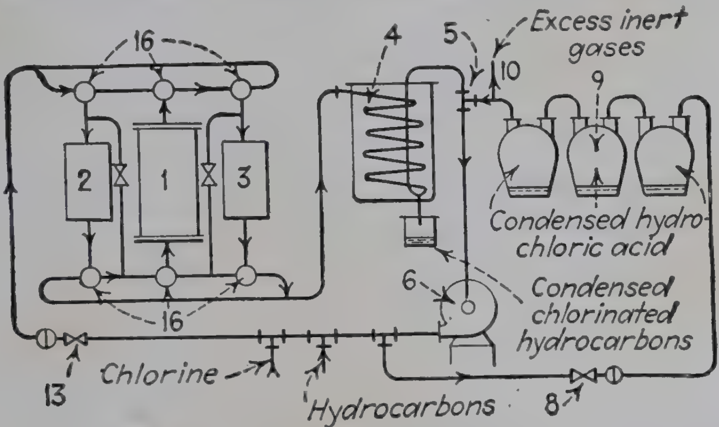
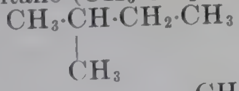
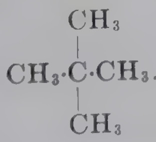

16
4
5
Excess inert gases
10
9
2
1
3
Condensed hydrochloric acid
6
Condensed chlorinated hydrocarbons
16
13
Chlorine
Hydrocarbons
8

Fig. 12.—Use of liberated hydrogen chloride as a diluent in chlorinations.

1. Reaction vessel.
2, 3. Heat exchangers.
4. Condenser.
5. Vent for excess hydrogen chloride.
6. Circulating fan.
8. Line to hydrogen chloride absorbers.
9. Absorbers.
13, 16. Circulating lines.

TECHNICAL HALOGENATIONS

Chlorination of Pentanes.—The process for the manufacture of amyl alcohols from pentanes was developed by Ayres.[2] The source of pentane is natural gas gasoline, the lower fractions of which yield the following pentanes:

	B.p., °C.
Normal pentane ($CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$)	36.0
Isopentane  $CH_3{\cdot}\underset{\underset{\displaystyle CH_3}{|}}{CH}{\cdot}CH_2{\cdot}CH_3$	28.0
Tetramethylmethane  $CH_3{\cdot}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{\cdot}CH_3$	9.5

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[1] U. S. 1,889,157 (1932).

[2] Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); U. S. 1,741,393 (1929); 1,835,202 (1931).

The reactions involved in this procedure may be simply expressed as follows:

$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$
$$C_5H_{11}Cl + NaOH \rightarrow C_5H_{11}OH + NaCl$$

Since there are three pentanes, eight possible amyl chlorides, and therefore eight arrangements of the alcohol $C_5H_{11}OH$, the process is not so simple as indicated in the equations above. In the commercial synthesis, normal pentane and isopentane (2-methyl-butane) are submitted to chlorination and subsequent hydrolysis. The vapors from the hydrolyzed material may be separated by a train of fractionating columns into five components, *viz.*, (1) amyl chloride, which is returned for hydrolysis; (2) amylene, which is later hydrated to amyl alcohol; (3) diamyl ether; (4) amyl alcohol fractions that are used for special purposes; and (5) the mixture of amyl alcohols marketed under the name of "Pentasol" for use as a solvent in the preparation of pyroxylin lacquers.

Previously in this chapter, emphasis has been placed upon the fact that chlorine does not readily attack the paraffin hydrocarbons unless considerable external energy in the form of heat—200 to 300°C.—is applied. Once initiated, however, the reaction is so vigorous that it is difficult to control unless special precautions are taken. When chlorine is added to an excess of pentane vapor flowing at the rate of 10 miles per hr., there is no tendency to ignite at temperatures up to 100°C., provided the ratio of pentane to chlorine is not less than 10:1. At lower ratios, ignition will be spontaneous, the combustion yielding carbon in the form of soot and hydrogen chloride:

$$C_5H_{12} + 6Cl_2 \rightarrow 5C + 12HCl$$

If the velocity of the admixed pentane is now increased to 30 miles per hr., the chlorine flame can be blown out. These phenomena are advantageously used in the process to be described.[1]

The chlorination of pentane is accomplished in equipment represented diagrammatically in Fig. 13, as follows: Pentane (normal or iso) is introduced into the system and is saturated with hydrogen chloride from the cycle of operations. The hydrocarbon is pumped at 75 lb. gauge pressure through a heater and vaporized at 85°C. It then passes into a venturi throat where it comes into contact with chlorine vapors which are supplied at 50°C. and 60 lb. pressure. At this point, the velocity of the pentane vapors should be above 60 miles per hr., and the volume ratio of hydrocarbon to chlorine about 15:1. When these conditions are observed, there is no danger of ignition when the combined vapors are led through the heat exchanger and the reactor. The reaction vessel is controlled at 250 to 300°C. The chlorine-free reaction gases pass through the heat

[1] U. S. 1,741,393 (1929); 1,831,474 (1931); 1,835,202 (1931).

exchanger and a cooler before entering a rectifying tower. The rectifier is supplied with a large body of refluxing pentane and chlorinated pentane from the dephlegmator. The refluxing mixture serves to condense most of the organic compounds but permits the hydrogen chloride and some uncondensed pentane to pass on. These residual gases are cooled and bubbled through pentane entering the system. The hydrogen chloride combines with any moisture in the paraffin hydrocarbon and is separated as hydrochloric acid by agglomerization and decantation.

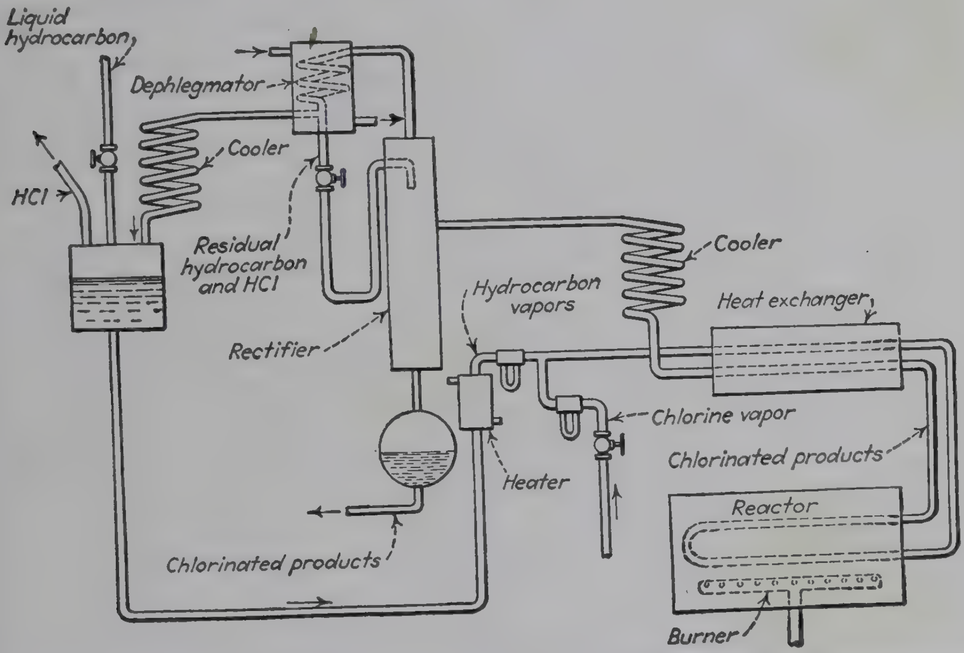
Liquid hydrocarbon
Dephlegmator
Cooler
HCl
Residual hydrocarbon and HCl
Rectifier
Cooler
Hydrocarbon vapors
Heat exchanger
Chlorine vapor
Chlorinated products
Heater
Reactor
Chlorinated products
Burner

FIG. 13.—Plant layout for chlorination of pentane and other paraffin hydrocarbons.

Any amyl chloride returned to the reaction zone immediately becomes an amylene dichloride. The reactions are quantitative, because the amyl chlorides are in equilibrium with amylenes and hydrogen chloride, and the fixation of the amylenes with chlorine causes the decomposition of amyl chlorides to be rapid and complete:

$$C_5H_{11}Cl \rightleftharpoons C_5H_{10} + HCl$$
$$C_5H_{10} + Cl_2 \rightarrow C_5H_{10}Cl_2$$

Even with a 15:1 hydrocarbon-to-chlorine ratio, about 5 per cent dichloride is formed.

According to Hass, chlorination of the pentanes yields all possible isomers; and, when the reaction is carried out at 300°C., the following ratios are obtained.[1]

From *n*-pentane: 24 per cent primary, 76 per cent secondary.

From isopentane: 50 per cent primary, 28 per cent secondary, 22 per cent tertiary.

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[1] HASS, MCBEE, and WEBER, *Ind. Eng. Chem.*, **28**, 333 (1936).

Preparation of Monochloroacetic Acid.—Monochloroacetic acid is prepared by passing chlorine through glacial acetic acid heated to 100°.C, red phosphorus being used as a catalyst.

The plant assembly may be arranged in the manner shown in Fig. 14. The acetic acid is stored in lead-lined tanks of any suitable size and is delivered as required to jacketed preheaters. The heated acid is run into a scale tank prior to delivery to the chlorinator. The chlorinator is a large, steam-jacketed vessel lined with heavy lead. The top of the vessel is equipped with connections for acetic acid, chlorine, air, effluent gases, condensate, discharge, and thermometer well. The jacket of the chlorinator is connected to both water and steam lines. The condensing system comprises a vertical reflux cooler through which the vapors rise and a return condenser to complete the condensation. The noncondensable gases are trapped out while the condensate is returned to the chlorinator below the surface of the reaction mixture.

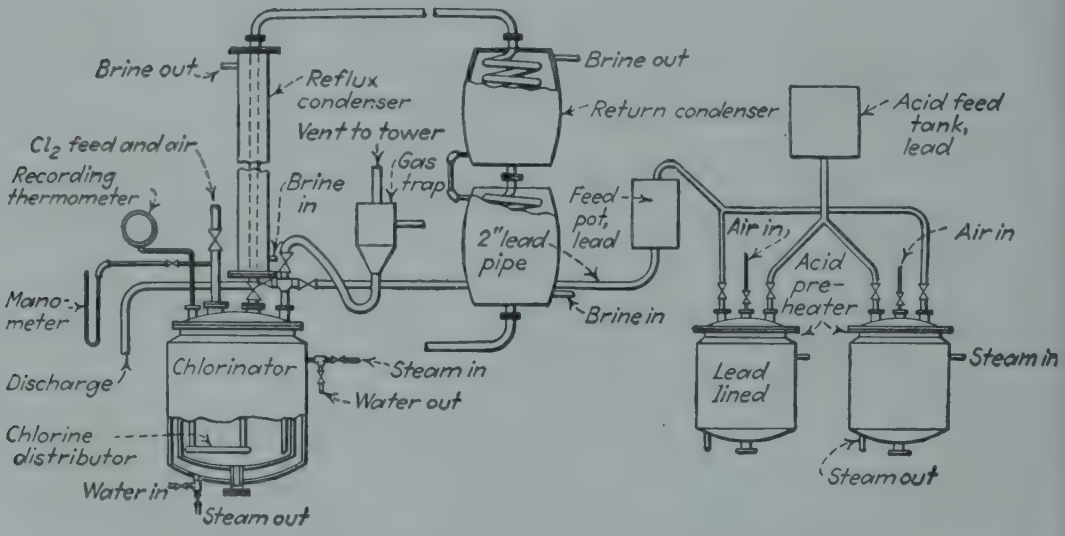

Brine out
Reflux condenser
Brine out
Return condenser
Acid feed tank, lead
Cl_2 feed and air
Vent to tower
Recording thermometer
Gas trap
Brine in
Feed pot, lead
2" lead pipe
Air in
Air in
Acid preheater
Manometer
Brine in
Steam in
Chlorinator
Steam in
Water out
Lead lined
Discharge
Chlorine distributor
Water in
Steam out
Steam out

FIG. 14.—Plant assembly, preparation of chloroacetic acid.

A charge consisting of 350 lb. of glacial acetic acid at 75°C. and 14 lb. of red phosphorus in 15 lb. of acetic acid is delivered to the chlorinator. The quantity of red phosphorus necessary for reaction diminishes with succeeding runs, so that 12 and 10 lb. may subsequently be employed. Chlorine is now admitted at the rate of 20 lb. per hr. At the end of the first hour, the rate is increased to 40; and at the end of this period, it is raised to 60 lb. per hr. and thus maintained throughout the remainder of the run. The heat of reaction brings the temperature of the charge up to 95 to 105°, at which range it is held by the use of either water or steam in the jacket of the chlorinator.

During the first part of the run, the circulation of brine through the reflux condenser system must be limited to avoid crystallizing the acetic acid. As chlorination proceeds, the quantity of acetic acid distilling off decreases, and the circulation of brine can be increased accordingly. Since the reflux condenser prevents the passage of any considerable quantity of acetic acid vapors from reaching the return condenser, the latter may be kept at approximately 0°C. to ensure the condensation of acetylchloride.

The results of operations, according to the preceding method, are shown in Table X.

TABLE X.—PREPARATION OF CHLOROACETIC ACID

Run	Acetic acid, lb.	Cl_2, lb.	Time of chlorination, hr.	Weight of chlorination mass, lb.	Yield based on acetic acid, %
1	350	425	11	472	85.7
2	350	480	9	503	91.1
3	350	485	12¼	512	93.0
4	350	425	8⅓	448	81.5
5	350	430	7¾	448	81.5
6	350	425	8	462	84.0
7	350	485	8	487	88.5
8	350	435	7	459	83.5

From the preceding data, it is evident that the best yields are obtained in those runs in which a liberal excess of chlorine is introduced over a longer period of time.

Chloroacetyl Chloride.—Chloroacetyl chloride is prepared by passing chlorine through a mixture of chloroacetic acid and sulfur monochloride at 45°C. Anhydrous zinc chloride is used as a catalyst. After the chlorination is complete, the chloroacetyl chloride (b.p., 105 to 106°C. at 760 mm.) is distilled from the mass as a colorless liquid.

The complete reaction involved in the preparation of chloroacetyl chloride is expressed by the following equation:

$$4CH_2Cl{\cdot}COOH + 3Cl_2 + S_2Cl_2 \xrightarrow{ZnCl_2} 4CH_2ClCOCl + 2SO_2 + 4HCl$$

When chloroacetyl chloride is condensed with benzene according to the Friedel and Crafts reaction (see Chap. XII), the valuable lachrymator ω-chloroacetophenone is obtained.

The plant assembly may be arranged in the manner shown in Fig. 15. The chlorinator used in this operation is preferably tall and narrow. This type of vessel is conducive to more efficient chlorination, because the time of contact between the chlorine and chloroacetic acid is increased. The chlorinator is lined with heavy lead and may be provided with a lead coil inside the reactor, connected to both steam and water to control the temperature. When jacketed vessels are employed, the lower heat transfer necessitates the maintenance of a considerable temperature gradient. Here, however, there is no danger of water's entering the reaction and ruining the charge because of a faulty coil.

The top of the chlorinator is equipped with connections for chlorine and air, chloroacetic acid and zinc chloride, sulfur monochloride, effluent gases, return line for condensate, and a thermometer well. At the base of the vessel is a flanged opening for cleaning purposes.

The chloroacetic acid (448 lb.) and zinc chloride (15 lb.) are put into the kettle through a large-flanged opening, and the required quantity of sulfur chloride (200 lb.) is then introduced. The chlorinator is closed, and steam is turned into the jacket or internal coil. When the temperature of the mass reaches 40°C., chlorine is introduced at the rate of 40 lb. per hr. The heat of reaction brings the temperature up to 45°C., and it is maintained at this point by circulating steam or water through the heat-transfer medium. At the end of the first hour, the rate of flow of chlorine is increased to 60 lb. per hr., and this rate is maintained until chlorination is complete. When the run is finished, the charge is transferred to a still.

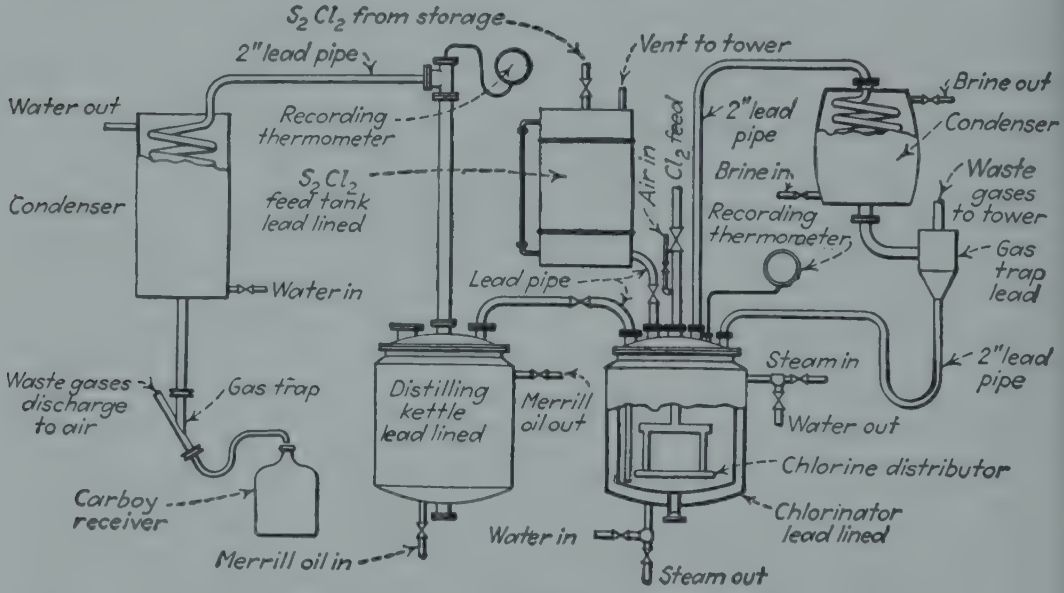

S_2Cl_2 from storage
2" lead pipe
Vent to tower
Water out
Recording thermometer
Condenser
S_2Cl_2 feed tank lead lined
Air in
Cl_2 feed
2" lead pipe
Brine in
Recording thermometer
Brine out
Condenser
Waste gases to tower
Gas trap lead
Water in
Lead pipe
Steam in
2" lead pipe
Waste gases discharge to air
Gas trap
Distilling kettle lead lined
Merrill oil out
Water out
Chlorine distributor
Carboy receiver
Chlorinator lead lined
Water in
Merrill oil in
Steam out

FIG. 15.—Plant assembly: preparation of chloroacetyl chloride.

The still is a lead-lined, jacketed vessel, the jacket being connected for high-pressure steam or a circulating fluid. The cover is provided with openings for charging and for effluent gases, a manhole for inspection purposes, and a well for a recording thermometer. A bottom flanged outlet is used when cleaning out the still. The distilled gases travel through a vertical dephlegmating column to effect a sharp separation of the fractions. The condensate is led to several receivers, and the uncondensed gases may be recovered in a suitable absorption system.

The first stages of distillation should be carried on slowly in order to get a satisfactory fractionation. The distillate obtained up to 90°C. (column temperature) is, after an analysis has been made for sulfur monochloride and dichloride, used again in the chlorination process. The second fraction, distilling between 90 and 102°C., is reserved for redistillation. The bulk of the charge, which distills between 102 and 110°C., is principally chloroacetyl chloride.

The presence of acetic acid to any appreciable extent has a tendency to lower the yields. The presence of sulfur as sulfur chlorides may be found in the chloroacetyl chloride, particularly when the fractionation is not satisfactory. The sulfur later exercises a deleterious effect if the chloroacetyl chloride is condensed with benzene to form chloroacetophenone.

TABLE XI.—PREPARATION OF CHLOROACETYL CHLORIDE

Run	Monochloroacetic acid, lb.	Acetic in chloroacetic acid, %	$ZnCl_2$, lb.	S_2Cl_2, lb.	1st and 2d fractions, lb.	Chloroacetyl chloride, lb.
1	448	0	15	190	55	378
2	446	0	15	199	103	380
3	448	0.31	15	190	45	385
4	449	Trace	15	200	110	395
5	444	0.33	15	200	75	375
6	447	0	15	200	91	379
7	443	0.30	30	210	68	382[1]
8	448	0.09	30	200	80	393

[1] The quantity of $ZnCl_2$ employed is generally increased in the first run following the cleaning of the chlorinator.

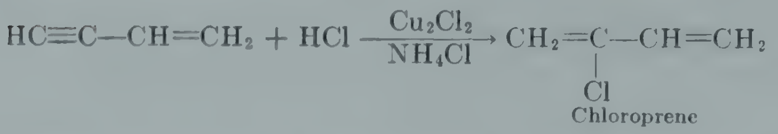
In Table XI are shown data relating to the preparation of chloroacetyl chloride.

Preparation of Chloroprene (2-Chloro-1, 3-butadiene).[1]—Chloroprene is obtained by passing monovinylacetylene into a cold aqueous solution containing hydrogen chloride and a cuprous chloride-ammonium chloride catalyst. The reactions for the preparation of vinyl acetylene and chloroprene may be represented as follows:

$$2CH{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinylacetylene}}{HC{\equiv}C{-}CH{=}CH_2} \qquad (1)$$

---

[1] The literature on this subject is important and voluminous, and the student is particularly referred to: NIEUWLAND, CALCOTT, DOWNING, and CARTER, *J. Am. Chem. Soc.*, **53**, 4197 (1931); CAROTHERS, WILLIAMS, COLLINS, and KIRBY, *J. Am. Chem. Soc.*, **53**, 4204 (1931); BRIDGWATER, *Ind. Eng. Chem.*, **28**, 396 (1936); U. S. 1,811,959, 1,812,541, 1,812,542, 1,812,544, 1,812,849 (1931); 1,896,159, 1,896,160, 1,896,162 (1933); 1,950,430 to 1,950,442 (1934).



$$HC\equiv C-CH=CH_2 + HCl \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Chloroprene}}{CH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2} \qquad (2)$$

Vinylacetylene, which has a vapor pressure of 621 mm. at 0°C., is removed along with some acetylene and vinylchloride by distillation at low temperatures. When reaction (1) is permitted to continue, particularly at temperatures above 30°C., a number of condensation products, especially divinylacetylene, are obtained. The latter on polymerization gives the synthetic drying oil "S.D.O."

Chloroprene can be prepared[1] by adding 50 parts of cold vinylacetylene to a chilled mixture composed of 175 parts of concentrated hydrochloric acid (sp..gr., 1.19), 25 parts of cuprous chloride, and 10 parts of ammonium chloride. The reaction mass is warmed to 30°C. and stirred for a period of 2 hr. The chloroprene that is formed is obtained by distilling the reaction mixture by steam in partial vacuum (100 to 250 mm.).

Chloroprene is a colorless liquid (b.p., 59.4°C. at 760 mm.). It polymerizes spontaneously even in the absence of light, and it is consequently essential to incorporate stabilizing agents, *e.g.*, phenyl-β-naphthylamine, catechol, etc., to keep polymerization conditions under control. At first the chloroprene is converted to a stiff, colorless, transparent jelly which contains a considerable amount of unpolymerized 2-chloro-1, 3-butadiene. As polymerization proceeds, the jelly contracts in volume and becomes a resilient elastic mass resembling a completely vulcanized soft rubber.

The condensation of vinylacetylene with hydrogen chloride may also be carried out in the vapor phase.[2] A gas consisting mainly of hydrogen and containing about 10 per cent vinylacetylene (obtained by leading electric arc acetylene over a cuprous catalyst), together with 3 liters of hydrogen chloride, is passed over a catalyst consisting of active carbon laden with mercurous chloride which is maintained at 120°C. The gas mixture leaves the reaction chamber with a vinylacetylene content of about 3 per cent. In the course of 24 hr., 190 gm. of chloroprene and 5 gm. dichlorobutene are obtained. The unconverted vinylacetylene is condensed with the 2-chloro-1, 3-butadiene and is returned to the reaction chamber after distilling it off from the condensate.

The 3, 4-dichloro-1-butene formed in the preceding operation can be converted to chloroprene by dehydrochlorination with solid potassium hydroxide.[3] The reaction may be represented as follows:

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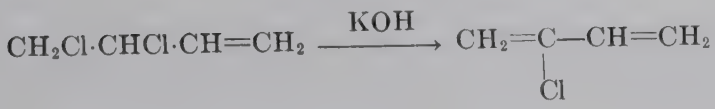
[1] CAROTHERS, WILLIAMS, COLLINS, and KIRBY, *loc. cit.*

[2] U. S. 2,098,089 (1937).

[3] U. S. 2,038,538 (1936).



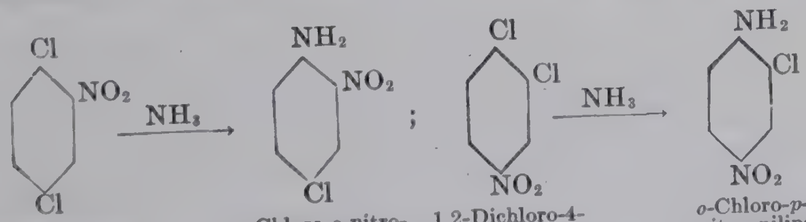
$$CH_2Cl\cdot CHCl\cdot CH=CH_2 \xrightarrow{KOH} CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2$$

Preparation of Chlorobenzenes.—The technical chlorination of benzene is carried out in glass-lined, lead-lined, or iron vessels. Wrought-iron particles or scrap pipe fittings are generally employed as the catalyst. When some anhydrous iron or aluminum chloride is added, the chlorination takes place more smoothly and without appreciable increase in the reaction temperature.

In the chlorination of benzene, the isomeric *o*- and *p*-dichlorobenzenes are found to accompany the principal monochloro compound. The reaction rate of benzene to chlorobenzene is approximately 8.5 times as great as that for chlorobenzene to dichlorobenzenes.[1] The relative yield of chlorobenzene improves with the speed or increase in rate of chlorination. Thus, when similar batches are treated at 25°C. for 3.5 and 5 hr., respectively, the former will contain about 6.51 per cent and the latter 8.05 per cent polychloro compounds at 74 to 75 per cent chlorination. Since the market and uses for dichlorobenzenes are limited, practical considerations sometimes decree the employment of less than the required molecular quantities of chlorine. Under such conditions, some benzene remains unreacted and is subsequently recovered upon distillation of the reaction mass.

Of the two isomeric dichlorobenzenes, the more valuable crystalline para compound (m.p., 53°C.) is formed in the largest quantities, the ratio of para to ortho being approximately 3:1. In most technical operations, the chlorination is continued until the benzene is all converted to the chloro derivatives. The composition of the charge will vary somewhat, depending on the temperature employed, the catalyst used, and the rate and degree of chlorination. The composition will be approximately as follows: chlorobenzene, 80 per cent; *p*-dichlorobenzene, 12 per cent; and *o*-dichlorobenzene, including polychloro compounds, 8 per cent.

p-Dichlorobenzene has found considerable use as an insecticide, moth repellant, and deodorant, whereas the ortho isomer has been used principally to combat termites and as a solvent. Nitration of the dichlorobenzenes followed by amination by ammonolysis leads to the formation



o-Nitro-*p*-dichlorobenzene

p-Chloro-*o*-nitroaniline

1.2-Dichloro-4-nitrobenzene

o-Chloro-*p*-nitroaniline

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[1] BOURION, *Compt. rend.*, **170**, 1309 (1920).

of useful dye intermediates. When these compounds are submitted to amination by reduction, diamino compounds are obtained.

Procedure.—The chlorination of benzene is generally carried out in tall cast-iron or steel tanks which preferably have been lined with a bonded lining of pure lead. The chlorinators are provided with a reflux condenser or an outside cooling system through which the charge may be circulated. When circulation of the chlorinated charge is effected by an external pumping system, it is not necessary to have an agitator in the reactor. All the auxiliary apparatus for stirring, cooling, and pumping should be lined with lead.

The chlorine is delivered through a distributor near the base of the reactor. The distributor may consist of a fused silica tube suitably perforated, or it may be made of a heavy-walled, seamless tubing which is inserted from a convenient opening in the top of the vessel. It may also be attached to a hollow, glass-lined shaft which serves as a stirrer as well as the inlet for chlorine. When an iron distributor is used, it offers a contact surface for catalysis and is readily attacked, and it therefore needs to be replaced periodically.

Approximately 12,000 lb. of dry benzene is delivered to the chlorinator. A small quantity of finely divided iron may be added, the amount depending on the quantity of catalyst retained in the chlorinator. In most technical operations, the bulk of the iron is retained in the system, either in the dished bottom of the chlorinator or in the shelves of the catalyst chamber superimposed on the chlorinator (Fig. 16). The former procedure permits operating at slightly higher temperatures, since the condenser and dephlegmator return any condensable vapors to the chlorinator. When the chlorinated benzene is circulated through a condenser located on the outside, the temperature of the solution when in contact with the catalyst must obviously be lower.

Chlorine is bubbled into the charge, the rate of feed being controlled so as to keep the temperature at the desired point. With outside circulation, the temperature of the chlorinated benzene is kept at 55 to 60°C. When a sample shows the required density, the current of chlorine is stopped. When all the benzene is to be chlorinated, the operation ceases when the density is 1.280 at 15°C. The time consumed is approximately 6 hr.

The hydrogen chloride that escapes through a vent in the dephlegmating or condensing system is washed with chloro- or *o*-dichlorobenzene to remove any organic spray that has been carried away.[1] The scrubbed gas is absorbed in a suitable absorption system.

Neutralization.—The chlorinated benzene is permitted to settle and then drawn off from a side outlet and delivered to the neutralizer. This may be vertical, jacketed, steel tank equipped with a reflux or condenser and a vent. A solution of caustic soda is added to the chlorinated benzene as it enters the neutralizer to provide a distinct alkaline reaction to litmus. It is necessary to mix the charge thoroughly to ensure neutrality, and agitation with a corrosion-resistant propeller or turbine type of stirrer is preferred. The charge is kept warm by jacket steam during the neutralizing treatment.

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[1] U. S. 1,858,521 (1932).

When repeated tests indicate a faintly alkaline reaction, the chlorinated benzene is delivered to a settling tank and permitted to stand for several hours. The sludge that settles out at the conical base is rich in dichlorobenzenes. The bulk of the charge is withdrawn through a side outlet and pumped to a storage tank, which is heated to prevent crystallization of the charge.

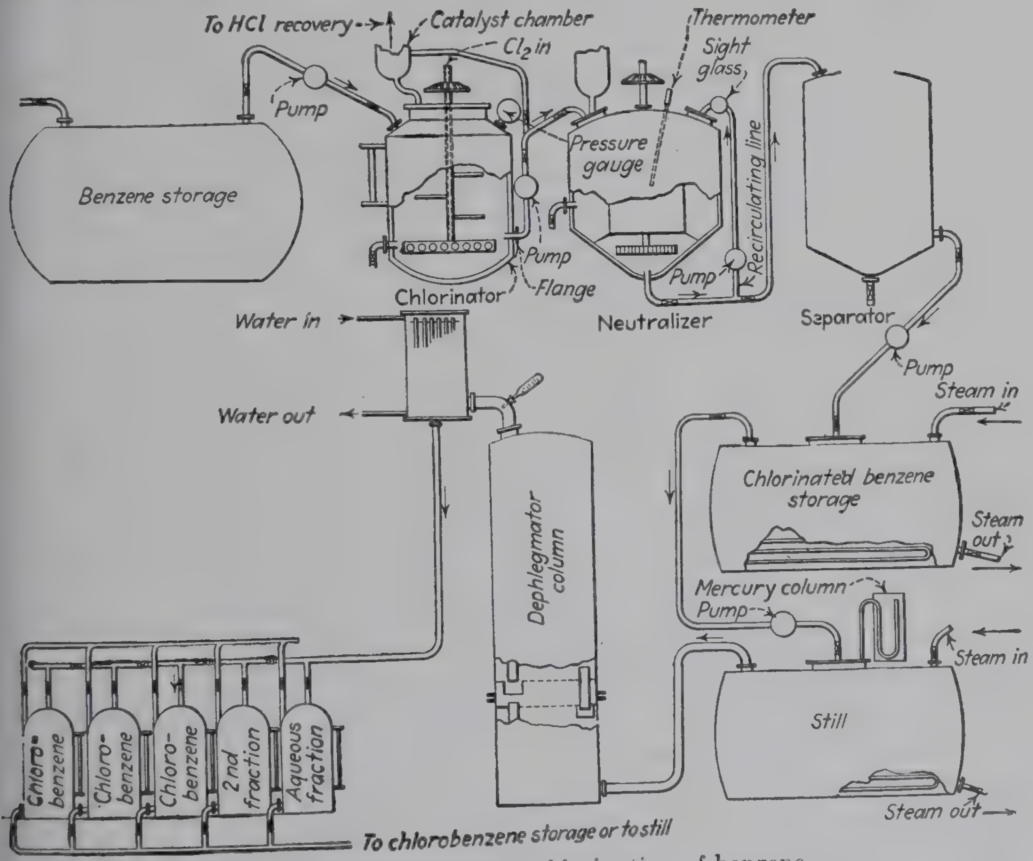
To HCl recovery
Catalyst chamber
Cl_2 in
Thermometer
Sight glass
Pump
Pressure gauge
Recirculating line
Benzene storage
Pump
Flange
Pump
Chlorinator
Neutralizer
Separator
Water in
Water out
Pump
Steam in
Chlorinated benzene storage
Steam out
Dephlegmator column
Mercury column
Pump
Steam in
Still
Steam out
Chloro-benzene
Chloro-benzene
Chloro-benzene
2nd fraction
Aqueous fraction
To chlorobenzene storage or to still

Fig. 16.—Plant assembly: chlorination of benzene.

The purification system comprises a horizontal still along with a dephlegmating and condensing apparatus. The chlorinated benzene is heated by steam coils and refluxed until the system is warm. The vapors are then drawn through a tall Kubierschky column to the condenser by a vacuum pump. The first fraction consists of benzene and water. The second fraction (sp. gr., 1.090 to 1.108 at 15°C.) is impure chlorobenzene and is added to the batch next to be distilled. The chlorobenzene fraction (sp. gr., 1.108 at 15°C.) is then run into separate containers. The presence of *p*-dichlorobenzene in the distillate is indicated by a sudden increase in the density of the distillate. The point is watched closely to prevent contamination of the principal product.

The residue in the still is principally dichlorobenzenes. This may be withdrawn after each charge or mixed with subsequent batches of chlorinated benzene until a sufficient quantity of it is accumulated. The para isomer, which has a slightly lower boiling point, can be recovered in a fairly pure state by fractional distillation. The residual ortho compound is contaminated with the para isomer and polychloro derivatives, principally 1, 2, 4-trichlorobenzene.

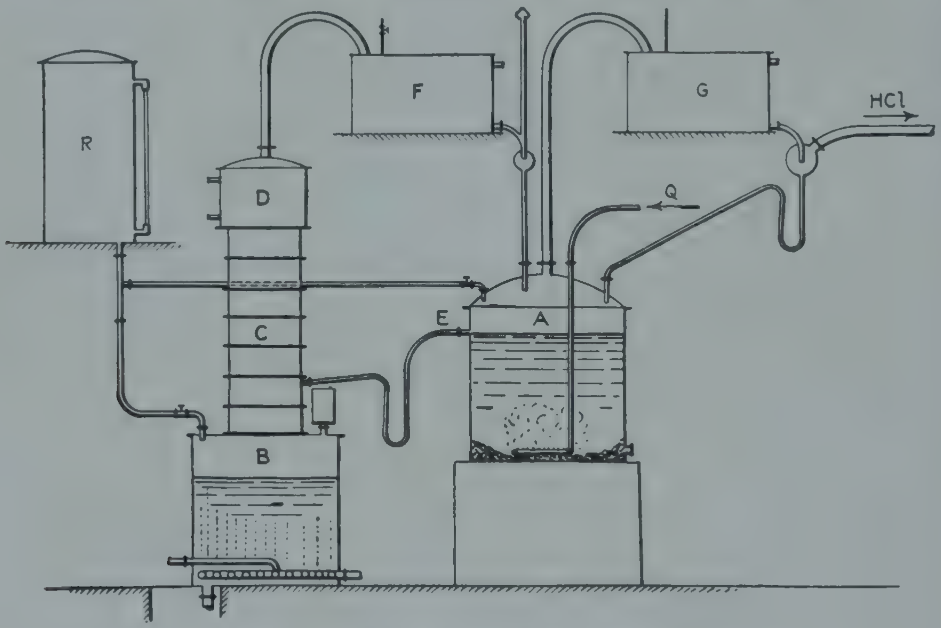

Fig. 17.—Plant layout: continuous chlorination of benzene.

A. Chlorinating vessel.
B. Heating chamber.
C, *D*. Fractionating column.
E. Overflow from chlorinator.
F. Condenser.
G. Scrubber.
Q. Chlorine inlet.
R. Benzene reservoir.

When the market for dichlorobenzenes is so restricted that it is not desirable to chlorinate all the benzene, the chlorination may be carried out as follows:[1] To reduce the formation of higher chlorinated products to a minimum, it is necessary to employ a large excess of benzene, and it is advisable, in order to avoid the handling of large volumes, to combine the chlorinating with a fractionating apparatus (Fig. 17). By this means, the monochlorobenzene is isolated as rapidly as it is formed, and only fresh benzene is exposed to the action of the chlorine. A portion of the benzene is introduced into the heating chamber of a fractional distillation unit *BCD*. This plant is completely lined with lead, and the column *C* s filled with Raschig rings. A second portion of benzene is delivered nto the lead-lined chlorinating vessel *A*, which is provided with a circular perforated pipe for the distribution of the chlorine. About 1 per cent by weight of iron turnings is used as the catalyst. The benzene in the chlorinator is brought to a boil by means of a closed steam coil. The condensed vapors return to the vessel, and then the partially chlorinated material runs through an overflow pipe *E* into the heating chambers of the distillation unit where it is fractionated, the benzene returning to the chlorinator.

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[1] Barthelmy, *Rev. prod. chim.*, **25**, 693 (1922).

The operation is continuous and is considered completed when the material in the fractionating still boils at 118 to 120°C. The material is then transferred to a vat containing a 10 per cent aqueous solution of caustic soda. The mixture is agitated mechanically for some time and then allowed to settle for a few hours. The aqueous portion is removed by decantation, and the crude chlorinated benzene rectified. The fraction between 80 to 90°C. is returned to the chlorination plant; the portion between 90 and 132°C. is redistilled with the next charge. The distillate coming over between 132 and 133°C., which constitutes about 70 per cent of the whole, is monochlorobenzene.

Preparation of Chloral and DDT.—The chlorination of ethanol can be carried out best in equipment designed for liquid-gas reactions. A chemicalware tower, a steel tower lined with bonded, glazed tile, or a tall, jacketed glass-lined vessel connected with a packed reflux condenser may be employed. It is advantageous to have the height of the chlorinator about five times its diameter to ensure maximum contact between ethanol and chlorine. It is also desirable to let the chlorine-containing exit gases from the reflux condenser pass through a second vessel containing ethanol, which is subsequently delivered by gravity or otherwise to the chlorinator.[1]

The chlorination vessel is two-thirds filled with ethanol, and a metered stream of chlorine obtained from a chlorine cylinder on a scale is injected. The chlorine passes through a fritted glass or other disperser located at the base of the reactor. The temperature rises quickly because of the exothermic reaction and the heat of solution of the liberated hydrogen chloride. The flow of chlorine is then curtailed to reduce the initial space velocity from about 90 to 25 to 30, space velocity here being the ratio of the volume of gas (Cl_2 at S.T.P.) passing through the liquid volume of ethanol in unit time. Therefore, space velocity = volume of gas ÷ liquid volume of alcohol. The charge is subsequently warmed, if necessary, in order to maintain a reflux of alcohol. If an early rise in operating temperature is permitted, the ethyl hypochlorite formed (see equations below) is immediately decomposed, and a hazardous accumulation of a large quantity is avoided.

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[1] Groggins, "Unit Processes in Organic Synthesis," 1st ed., McGraw-Hill Book Company, Inc., 1934. See also *Chem. Met. Eng.*, p. 112, October, 1944.

The equations below indicate the need of 4 moles of chlorine per 2 moles of ethanol. In practice, a ratio of about 2.25:1 is used to compensate for unreacted chlorine leaving the system and to ensure complete chlorination.

$$\begin{aligned} &C_2H_5OH + Cl_2 &&\rightarrow C_2H_5OCl + HCl && (1)\\ &CH_3CH_2OCl + C_2H_5OH &&\rightarrow CH_3CH(OH)OC_2H_5 + HCl && (2)\\ &CH_3CH(OH)OC_2H_5 + 3Cl_2 &&\rightarrow CCl_3CH(OH)OC_2H_5 + 3HCl && (3)\end{aligned}$$

The equations also show that 2 moles of ethanol are required per mole of hemiacetal and, therefore, of chloral, and the yields are calculated on this basis.

The salient data pertaining to the chlorination operation are shown in Table XII below.

Table XII.—Operating Conditions: Chlorination of Ethanol

Charge ($C_2H_5OH + H_2O$), moles	5.6
Chlorine input, moles	14.0
Initial space velocity (average)	90
Operating space velocity (average)	25
Initial temperature, °C	22
Operating temperature, °C	78–95
Total time, hr	30*a* + *b*
a. Time, initial space velocity, hr	2
b. Time, operating space velocity, hr	28
Molal ratio chlorine to alcohol	2.25:1
Yield of chloral, %	83

The quantity of chlorine that escapes from the reactor is related to the operating technic and design of apparatus rather than to the concentration of ethanol. The loss of chlorine is ordinarily negligible until most of the theoretical quantity (2 moles per mole C_2H_5OH) of chlorine has been added. The chlorine gas in the exit gases then increases rapidly. The over-all unreacted chlorine is about 5 per cent.

The production of ethyl chloride as a coproduct occurs principally during the period when 0.5 to 1.7 moles chlorine per mole of ethanol have been introduced. This is the stage corresponding to the conversion of the ethyl hemiacetal to the trichloro derivative (see page 197). The quantity of ethyl chloride, as can be seen from the data in Table XIII, is related to the water content of the ethanol.

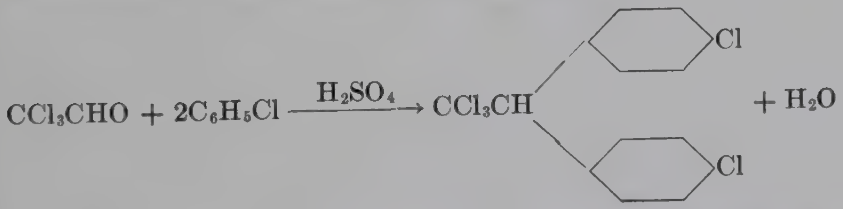
The product of chlorination, which is a mixture of chloral hydrate and chloral hemiacetal, is a clear, yellow, viscous oil (sp. gr., 1.50 to 1.55). The reaction mixture is delivered to a glass-lined still where it is mixed with an equal volume of 80 to 85 per cent sulfuric acid. The distillation is carried out over the acid, and the fraction boiling between 93 and 98°

s taken as the chloral cut. The crude material can be used directly for the manufacture of DDT or can be purified by redistillation in the presence of calcium carbonate and fractionating in a plate column. The boiling point at 320 and 760 mm. are 69.6 and 97.7°, respectively.

TABLE XIII.—RELATION OF ETHANOL CONCENTRATION TO YIELDS OF ETHYL CHLORIDE AND CHLORAL

Expt. No.	C_2H_5OH, % by wt.	C_2H_5Cl, yield, moles	Moles H_2O/mole C_2H_5OH	Moles C_2H_5Cl/mole C_2H_5OH	Chloral yield, %
1	100	0.78	0	0.14	77.61
2	95	0.86	0.14	0.15	83.30
3	90	0.78	0.29	0.14	83.00
4	85	1.27	0.45	0.23	73.10
5	80	2.03	0.64	0.36	65.10
6	75	1.61	0.85	0.29	59.00
7	70	1.06	1.10	0.20	57.15
8	65	0.08	1.40	0.01	57.20

DDT 1-Trichloro-2, 2-bis-(*p*-chlorophenyl) Ethane.—DDT[1] is the contraction for that class of compound known generically as dichlorodiphenyl-trichloroethane which is obtained when chloral is condensed with chlorobenzene in the presence of sulfuric acid.[2]



In the absence of chloral, the sulfonation of chlorobenzene is extensive at the same temperatures and concentrations commonly employed for the condensation. In spite of this fact, the yield of DDT is high, indicating that under properly chosen conditions the DDT condensation is faster than the sulfonation reaction. In general, the more concentrated acids at lower temperatures favor the condensation reaction over the sulfonation reaction, whereas more dilute acids at higher temperatures favor sulfonation over condensation.

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[1] Based extensively on O.S.R.D. research by M. R. Cannon and H. S. Mosher, Pennsylvania State College. See also Report No. 240 O.P.B.

[2] Theoretically, there are a large number of possible isomers and related products that can be obtained by this condensation. Already, 14 of such compounds have been isolated by Haller and coworkers. HALLER *et al.*, *J. Am. Chem. Soc.*, **67**, 1591 (1945); CRISTOL and HALLER, *Chem. Eng. News*, **23**, 2070 (1945). The para para isomer, or p, p′-DDT, melts at 108.5 to 109.0° and constitutes about 70 to 75 per cent of the product. The o, p′-DDT which melts at 74.0 to 74.5° is found to the extent of 19 to 21 per cent. The minimum *setting* point of the technical grade acceptable for insecticidal preparations is 89°. The melting point of a purified material for use in aerosols should be not less than 103°. From the standpoint of insecticidal properties, the p, p′-DDT is the most effective. CRISTOL and HALLER, *ibid.*

The optimum operating acid concentration for DDT condensation is approximately 98 to 99 per cent sulfuric acid. With this concentration—and the amount of acid indicated below—the operating temperature should be approximately 20°. Accordingly, 200 parts of 99 per cent sulfuric acid, 74 parts of chloral, and 124 parts or more of chlorobenzene are introduced into a jacketed, glass-lined reactor. While the reaction temperature is maintained at 20° by jacket cooling, 178 parts of 104 per cent oleum is added and the mixing continued for an additional 5 hr.

When the condensation is carried out substantially as above but with varying temperatures, the yield and setting point of the DDT are markedly affected, as is evidenced by the data in Table XIV.

TABLE XIV.—PER CENT YIELD AND SETTING POINT OF DDT AT VARIOUS TEMPERATURES USING 98 PER CENT SULFURIC ACID* AND 6 HR. REACTION TIME

Temp., °C.	Setting point, °C.	% yield
5	84	81
15	89	86
25	88	84
35	84	75
45	82	67
55	82	45

* Calculated final acid concentration.

Instead of the acid concentrations noted above, some manufacturers initiate the condensation with 1 part by weight of 93 per cent sulfuric acid and then add 20 per cent oleum at a 3:1 ratio by weight to the chloral content. Glass-lined equipment or steel vessels lined with pyroflex and a single course of tile or brick should be used throughout, unless special purification procedures are to be employed. Catalytic amounts of iron initiate the reaction;

$$CCl_3CH(C_6H_5Cl)_2 \rightarrow CCl_2{=}C(C_6H_5Cl)_2 + HCl$$

An excess of chlorobenzene is conducive to higher yields (92-98 per cent) and is used for the condensation when it is to be employed as the extractant for the DDT in subsequent operations.

Isolation of DDT.—The crude DDT can be isolated from the reaction mixture by a number of technics, including solvent extraction with petroleum fractions, with excess of chlorobenzene, or by filtration.

In the solvent-extraction process, 0.5 liter of *n*-hexane (or *n*-hexane-methylcyclohexane mixture, b.p., 68°) per mole of DDT is added to the reaction mixture. The DDT and impurities are extracted at 60°, and the sulfuric acid drawn off. The hexane solution is then washed successively with water, 2 per cent sodium carbonate, and water, using about 0.25 liter of wash water per mole of DDT content. The resultant solution is heated above the melting point of the crude DDT (about 105°), and the solvent distilled. The last traces of hexane can be removed under reduced pressure, after which the molten DDT is drained onto a stainless steel flaker or glass-lined crystallizing equipment.

In the filtration purification process, the DDT is separated directly (or after dilution with water to about 80 per cent H_2SO_4 concentration) from the reaction mixture by filtering through glass cloths. The crude DDT, which is obtained as needlelike crystals, is then transferred to a kettle where it is washed while stirring successively with water, a sodium carbonate solution, and finally with water. The charge is cooled, filtered from wash waters, and then dried. This procedure gives a product having a setting point of 90 to 92°, but the yield is about 80 per cent, which is lower than that obtained by other purification processes. The filtered sulfuric acid containing dissolved impurities may be used in conjunction with the distillation of the hemiacetal of trichloroacetaldehyde.

In the "Brothman" continuous process, an excess of chlorobenzene is used during the condensation. The reaction mass is delivered to a stoneware tower in which the sulfuric acid is separated from the DDT-chlorobenzene suspension.[1] By means of a balance leg, the heavier acid is withdrawn at the base while the dissolved DDT is continuously removed at the top of the tower. The DDT suspension is led to a series of three towers where it is scrubbed successively by countercurrent washing with water, dilute sodium carbonate, and again with water.

The chlorobenzene is removed from the DDT by distillation at 35 mm. pressure and 105°. This temperature is necessary to keep the DDT, now freed of solvent, in a liquid state. The chlorobenzene is condensed and returned to the operating cycle.

The molten DDT from the stripping still which contains significant amounts of chlorobenzene is delivered to a similar still provided with propeller-type agitation and operating at atmospheric pressure. Here the charge is maintained at 105°; and by means of a current of air delivered into the agitated mass, all but a trace of chlorobenzene is removed. The molten DDT is run into a steam-heated feed trough and thence onto a rotating drum flaker. The flaked material is pulverized to pass through a 150-mesh sieve.

It is estimated that the net cost of production is less than 30 cts. per lb. of DDT. Raw materials account for almost 75 per cent; steam, water, electricity, and labor account for about 8 per cent; and overhead accounts for about 17 per cent of the total cost.

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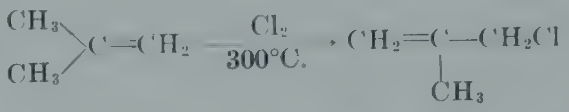
[1] CALLAHAM, staff report, *Chem. Met. Eng.*, **51**, No. 10,109 (1944).

Preparation of Methallyl Chloride.[1]



$$\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C{=}CH_2 \xrightarrow[300^\circ C.]{Cl_2} CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CH_2Cl$$

The operation is conducted in the apparatus shown diagrammatically in Fig. 18. Isobutylene is delivered from a storage tank through a meter to a preheater 2 and thence to a branched mixing tube 3, where it comes in contact with chlorine gas delivered from cylinder 4. The flow of chlorine is controlled by valves so that about ⅔ mole is introduced per mole of isobutylene. The mixed reactants pass through a reaction tube 5, at such a rate that the time spent in this zone at 300°C. is less than 1 sec. The reaction products are conducted directly to the base of a hydrochloric acid scrubbing tower 6, which is packed with ceramic rings. Water or dilute hydrochloric acid is admitted at a rate sufficient to form a 5 to 10 per cent HCl solution at the bottom of the column. The unre-

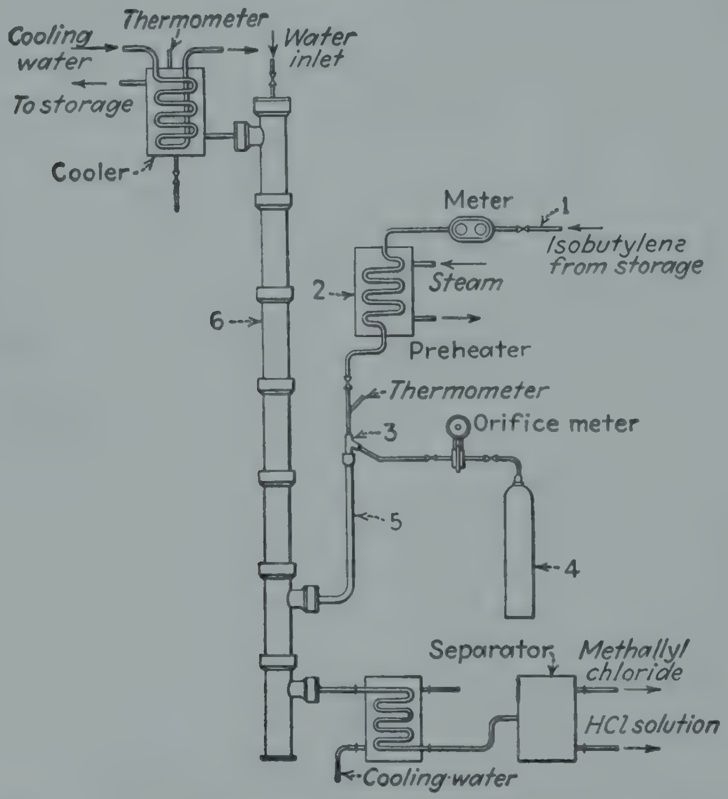

Thermometer
Cooling water
Water inlet
To storage
Cooler
Meter
1
Isobutylene from storage
Steam
2
6
Preheater
Thermometer
3
Orifice meter
5
4
Separator
Methallyl chloride
HCl solution
Cooling water

FIG. 18.—Flow diagram, preparation of methallyl chloride.

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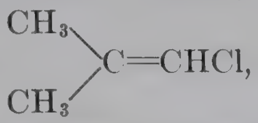
[1] Engs and Redmond, U. S. 2,077,382 (1937).

acted isobutylene, together with other hydrocarbons and some methylallyl chloride, pass to the top of the tower and thence through the cooler, where the methallyl chloride separates out. The methallyl chloride and dilute hydrochloric acid run from the bottom of the tower through a cooler to a separator. Here, the crude methallyl chloride, which is contaminated by isocrotyl chloride  $(CH_3)_2C{=}CHCl$, is separated and then purified.

Preparation of Ethylene Chlorhydrin.—The preparation of ethylene chlorhydrin may be carried out continuously in the apparatus shown in Fig. 19.[1] The tower is first charged with ethylene under a pressure of 200 atmos. at 20°C. A solution of hydrated lime is then introduced until the desired quantity collects at the base of the tower, compressed ethylene being admitted simultaneously in order to maintain the desired pressure. The alkaline solution of ethylene is then transferred at such a rate as to keep the solution level in the tower about constant. Under such operating conditions of temperature and pressure, about 28 gm. of ethylene per liter is in solution, compared with 0.14 gm. at normal temperatures and pressures. As the solution enters the mixer, chlorine is introduced at the rate of 1 mole (70.9 gm.) per liter. The quantity of lime in suspension in the tower is regulated at approximately half the molal concentration of the ethylene in solution leaving the tower—in this case, 0.5 mole, or 28 gm., of CaO per liter. In the mixer, the chlorine reacts with the hydrated lime to form calcium oxychloride. This compound is at once decomposed to form hypochlorous acid and calcium chloride.

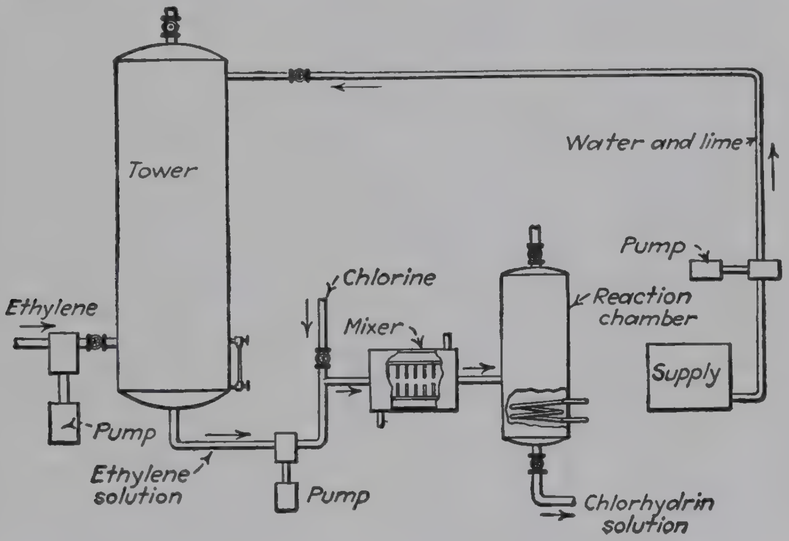


FIG. 19.—Plant assembly: preparation of ethylene chlorhydrin.

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[1] Youtz, U. S. 1,875,309 (1932).

$$\text{CaO} + \text{Cl}_2 \rightarrow \text{CaCl·OCl}$$
$$\text{CaCl·OCl} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{CaCl}_2 + 2\text{HOCl}$$

The hypochlorous acid reacts with ethylene as the mixture traverses the reactor, forming ethylene chlorhydrin.

$$\text{HOCl} + \text{H}_2\text{C}{=}\text{CH}_2 \rightarrow \text{CH}_2\text{OH·CH}_2\text{Cl}$$

The ethylene chlorhydrin-calcium chloride solution is withdrawn from the reaction chamber. Such solutions may be treated directly with alkaline reagents for the preparation of glycol. Alternatively, the ethylene chlorhydrin may be recovered by distillation and subsequent salting out.

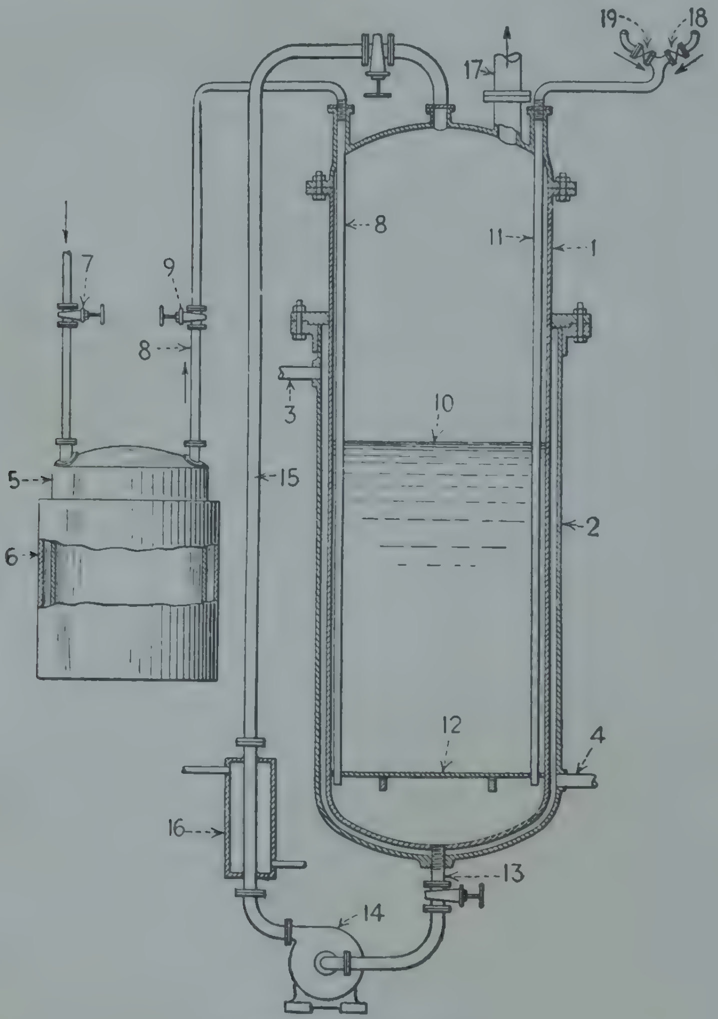

FIG. 20.—Apparatus for fluorination of CCl_4.

1, 2. Reaction vessel with jacket.
3, 4 Inlet and outlet to jacket.
5, 6. Hydrogen fluoride vaporizer with jacket.
7, 9. Control valves on inlet and outlet lines for HF.
8. Delivery line for HF.
10. SbCl_5 catalyst.
11. Internal delivery line for CCl_4.
12. Distributor plate.
13, 14, 15. Circulating line and pump.
16. Heat exchanger for steam.
17. Outlet for gaseous products.
19. 18, Control lines for fresh and recovered CCl_4.

Fluorination of Carbon Tetrachloride.—The preparation of difluorodichloromethane by the fluorination of carbon tetrachloride can be carried out in the apparatus shown diagrammatically in Fig. 20.[1] The operation is started by adding about 600 parts of antimony pentachloride to the cast-iron reaction vessel, which is maintained at 60°C. Over a period of 24 hr., 500 parts of dry hydrogen fluoride is delivered from the vaporizer through the steel line 8, while concurrently 1,925 parts of fresh carbon tetrachloride is introduced through lines 18 and 11. After the reaction is under way, the recovered CCl_4 from steel scrubbers is returned by way of line 19. During the reaction, the catalyst-containing reaction mixture is continuously circulated through the heat exchanger 16, maintained at 110°C., and is returned to the vapor space above the charge.

The vaporized products are hydrochloric acid, fluorotrichloromethane, and difluorodichloromethane, together with some unreacted hydrogen fluoride and carbon tetrachloride. These vapors are passed first to a warm and then to a cold carbon tetrachloride scrubber—the second refluxing back to the first. The residual gases are further purified by passing them through water, aqueous sodium hydroxide, and concentrated sulfuric acid and then subjecting them to condensation. Difluorodichloromethane is thus obtained in good yields.

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[1] U. S. 2,058,453 (1936).

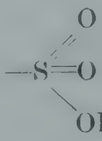
CHAPTER V

SULFONATION

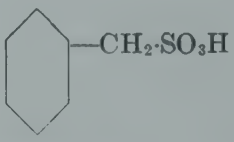
By P. H. Groggins and W. A. Simpson

I. INTRODUCTION

Definition.—Sulfonation may be defined as the process whereby the union of the group



to carbon or nitrogen of an organic compound is effected. In the aliphatic series, three sulfonic groups may be attached to the same carbon atom, as in methanetrisulfonic acid [$CH(SO_3H)_3$]. In the aromatic series, however, no sulfonic acid is known that has two such groups attached to the same carbon atom. In the aliphatic series, mono-, di- and trisulfonic acids can be obtained; and, in the aromatic series, even tetrasulfonic acids have been prepared. Combinations of aliphatic sulfonic acids attached to an aromatic nucleus also occur, as in toluene-ω-sulfonic acid.



The sulfonic acids of aromatic compounds are of much wider commercial importance than the aliphatic sulfonic acids. One of the distinguishing characteristics between aliphatic and aromatic compounds is the ease with which the aromatic unsubstituted hydrocarbons form sulfonic acids with moderately concentrated sulfuric acid, in contrast to the difficulty experienced with the lower saturated paraffin hydrocarbons. The latter require sulfuric acid containing free SO_3 (oleum) to effect substitution of the sulfonic acid group. Unsaturated aliphatic compounds, however, readily add on sulfuric acid, and this reaction is employed extensively in the commercial separation of olefins from the saturated components of petroleum.

With the steady development of new and inexpensive technics for the preparation of aliphatic sulfonic acids, these compounds are rapidly finding increased commercial uses, such as in the emulsification and dispersion of liquids, in the dispersion and wetting of solids, and as wetting agents.[1]

Of growing importance too are the sulfoarylstearic acids as well as the sulfoarylalkanes. The simpler arylstearic acids of the benzene series yield monosulfoarylstearates, the sodium salts of which have penetrant and emulsifying properties, and the free acids are fat-splitting agents. The use of sulfoarylalkanes as detergents is continuously expanding, because, in contrast to soaps, they are stable to hard water and toward alkaline and acid solutions. Such sulfonic acids in the form of the sodium salt (nacconol, santomerse, etc.) are used for the cleaning of fabrics, leather, paper, and felt and as a component of numerous cleaning or detergent powders.

The sulfonic acids are not to be confused with the esters of sulfuric acid or alkyl sulfuric acids of the general formula $RO \cdot SO_2 \cdot OH$, as for example ethyl sulfuric acid (ethyl hydrogen sulfate) $C_2H_5O \cdot SO_2 \cdot OH$, wherein SO_3H is linked to oxygen and not to carbon, as in ethylsulfonic acid ($CH_3 \cdot CH_2 \cdot SO_3 \cdot H$). A general distinguishing characteristic of the sulfuric acid esters is the ease with which they are hydrolyzed when boiled with dilute aqueous solutions of acids or alkalies; the sulfonic acids are ordinarily relatively stable under these conditions. Because of the extensive industrial utilization of the sulfuric acid esters of the higher fatty alcohols and their similar mode of preparation, such *sulfations* are also discussed in this chapter.

Uses of Sulfonic Acids.—One of the most important uses of sulfonic acids relates to their employment in the synthesis of intermediates for dyestuffs. By replacing the sulfonic acid group in aromatic compounds, it is possible to effect the preparation of hydroxy, nitro, amino, and halogeno compounds. A particular advantage of the sulfonic acid group is its property of conferring increased solubility of the compound in aqueous solutions, and it is this characteristic which facilitates the subsequent conversion or direct application of such compounds. In the chapter on amination by ammonolysis, it is shown that the replacement of $—SO_3H$ by $—NH_2$ takes place more readily than the similar replacement of $—Cl$.

Sulfonated castor oil, olive oil, and other vegetable oils have long been used in the textile, leather, paper, glue, and other industries. Certain sulfonic acids find special uses as follows:

1. As aids in leather treatment—employing the sulfonation products of phenol-aldehyde condensations.

2. As a constituent of soaps—using the alkali salts of sulfonated mineral oils.

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[1] Approximately 100,000,000 lb. of synthetic detergents, wetting agents, and similar surface-active materials was produced in the United States in 1945. Practically all these compounds were prepared by sulfonation or sulfation.

3. As wetting or emulsifying agents—introducing small quantities of sulfonated tetrahydrobenzene, propylene, trichloroethylene, butylnaphthalene, stearic, oleic, or palmitic acids, etc.
4. As aids in dyeing.
5. As detergents—derivatives of isethionic acid (hydroxyethylsulfonic acid) with oleic acid or its derivatives, the sulfoarylalkanes previously mentioned, and the sodium salts of sulfonic and chlorosulfonic acids of white oil (petroleum fraction sp. gr., 0.8033; b.p., 283 to 324°), which are obtained by the action of a mixture of SO_2 and Cl_2 on the hydrocarbon.[1]

Of great importance also and related to sulfonic acids are the sulfuric acid esters of cetyl, lauryl, stearyl, and palmityl alcohols which are used as detergents.

II. SULFONATING AGENTS AND THEIR PRINCIPAL APPLICATIONS

In the following paragraphs, a survey is made of the principal sulfonating agents and some of their technical applications. These agents may be listed as follows:

1. Sulfuric acid.
2. Oleum (solution of SO_3 in 100% H_2SO_4).
3. Sulfur trioxide alone.
4. Acid sulfates and polysulfates.
5. Chlorosulfonic and fluosulfonic acids.
6. Sulfur dioxide.
7. Sulfites and acid sulfites.
8. Hyposulfites (hydrosulfites).
9. N-Pyridiniumsulfonic acid.
10. Dioxane sulfotrioxide.
11. Aminosulfonic acids.
12. Sulfuryl chloride.
13. Dimethyl and diethyl sulfates.
14. Methoxysulfone chloride.

The choice of the agent and the technic employed will be governed by such factors as the chemical and physical properties of the organic compound as well as by the economics of competitive methods.

Sulfuric Acid

Properties.—In the sulfonation process, the chemical behavior of sulfuric acid is conditioned largely by its power for withdrawing water. Sulfur trioxide forms a number of well-defined hydrates with water.

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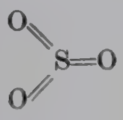
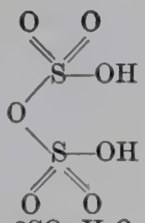
[1] Lockwood and Richmond, U. S. 2,193,824 (1940); Fox *et al.*, U. S. 2,202,791 (1940); see also chapter on Halogenation.

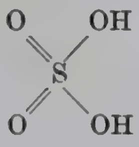
The principal hydrates coming within the category of sulfonating agents are the following:



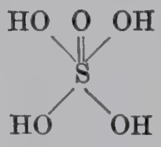
SO_3
Anhydride



$2SO_3 \cdot H_2O$
Pyrosulfuric Acid



H_2SO_4
Monohydrate



$H_2SO_4 \cdot H_2O$
Dihydrate

Tri- and pentahydrates of sulfur trioxide are also known, and this great affinity for water is evidenced by its hygroscopicity and its efficacy as a dehydrating agent in removing the elements of water from inorganic and organic substances.

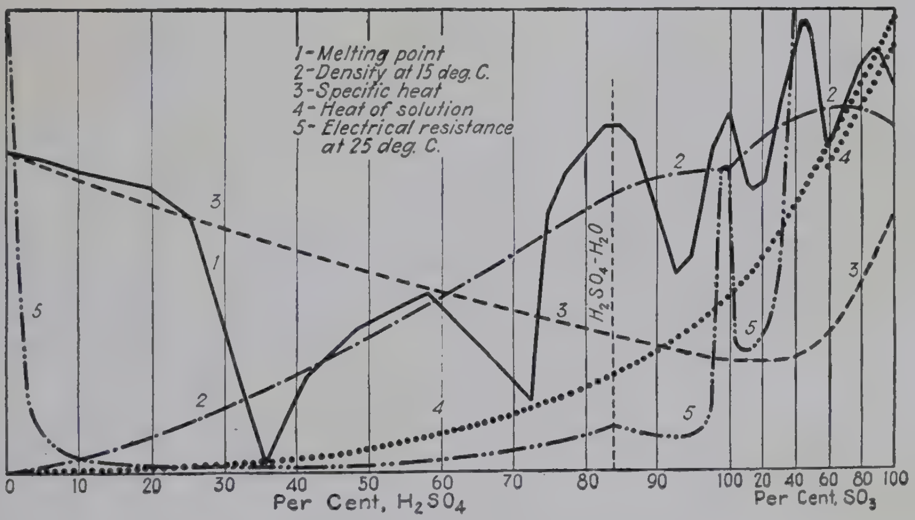


Fig. 1.—Physical properties of sulfuric acid.

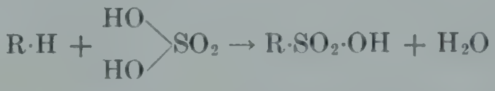
The hydrates of sulfuric acid exist at low temperatures as definite crystalline compounds; and, with rising temperature, they all decompose with more or less ease with the disengagement of either sulfur trioxide or water. In their ordinary form, they present all the properties of simple solutions, and it is permissible to presume that between SO_3 and H_2O there exists a consecutive series of homogeneous liquids or solutions among which are distinguished definite hydrates. In other words, the term *sulfuric acid* is the generic name of a series of solutions of sulfur trioxide in water, some of which are chemical hydrates of SO_3 and most of which are merely solutions of the gas of convenient strength for use in the arts.

When sulfuric acid and water are mixed, a considerable rise of temperature occurs (see Fig. 1). Experience has shown that the activity of sulfuric acid as a sulfonating agent is directly related to its concentration, and this governs the heat of solution and its driving power, *i.e.*, the capacity to withdraw the elements of water from the reacting compounds.

The vapor of sulfuric acid is completely dissociated into water and sulfur trioxide at 450°C. At ordinary temperatures, however, the gas is more or less bound up as hydrates; this union becomes weaker with increasing temperature. These properties of sulfuric acid thus lead to the belief that SO_3 dissolved in or combined with sulfuric acid may be the true sulfonating agent. It is known that sulfur trioxide, liquid or gaseous, can be employed for the preparation of sulfonic acids, the process being essentially one of addition, thus:

$$R{\cdot}H + SO_3 \rightarrow R{\cdot}SO_3H$$

The sulfonating action of sulfuric acid may be represented by the following equation:



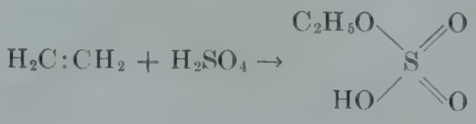
$$R{\cdot}H + (HO)_2SO_2 \rightarrow R{\cdot}SO_2{\cdot}OH + H_2O$$

Water is therefore a by-product, and it is known that with increasing H_2O concentration the rate of sulfonation is decelerated. The critical acid concentration is not the same for all sulfonations, for this depends on the temperature and particularly on the reactivity of the organic compound with sulfuric acid; and this characteristic is related to the type, structure, and substituents present in the compound undergoing treatment.

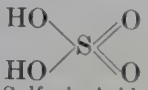
Treatment of Aliphatic Compounds with Sulfuric Acid.—Sulfuric acid does not react with the saturated paraffin hydrocarbons, and only by using oleum can the compounds containing 6 to 8 carbon atoms be converted directly to sulfonic acids.

$$C_6H_{14} \xrightarrow{\text{Oleum}} C_6H_{13}{\cdot}SO_3H + H_2O$$

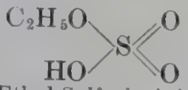
Sulfuric acid does, however, combine with olefinic compounds to form sulfates, and this reaction is employed in the preparation of alcohols



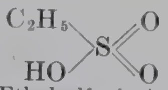
and in the technical separation of unsaturated hydrocarbons derived from petroleum cracking operations. This procedure, like the treatment of ethanol with sulfuric acid, results in the formation of alkyl sulfates or esters wherein a hydrogen atom rather than the hydroxyl group of the sulfuric acid is replaced. The following formulations serve to bring out this distinction:



Sulfuric Acid



Ethyl Sulfuric Acid



Ethylsulfonic Acid

Treatment of Aromatic Compounds with Sulfuric Acid. *Benzene Derivatives.*—The ease with which aromatic hydrocarbons react with sulfuric acid to form sulfonic acids is one of the characteristics that differentiate them from the paraffin hydrocarbons. Benzene, for example, can be sulfonated by adding to it 2.5 times its weight of 98 per cent sulfuric acid, heating at 80°C. until refluxing stops, and finally heating at 100°C. Completion of the reaction is indicated by the absence of benzene in a diluted sample of the reaction mass. The product can be converted to the calcium sulfonate by treatment with lime and filtering off the precipitated gypsum. The sodium sulfonate is obtained by treating a hot suspension of the calcium salt with the calculated quantity of soda ash or treating the sulfonation mass directly with sodium sulfite, when the latter is available as a by-product from the alkali fusion operations in the production of sodium phenoxide.

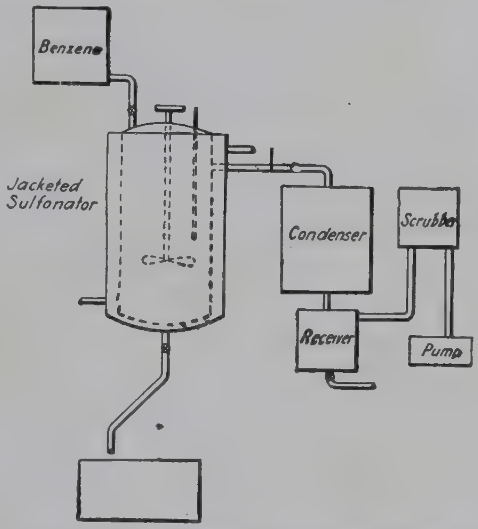


Fig. 2.—Plant assembly: disulfonation of benzene.

To prepare benzenedisulfonic acid, it is necessary to sulfonate at 220 to 260°C. When a considerable excess of sulfuric acid is employed, *i.e.*, about 300 per cent, a yield of about 90 per cent of the theoretical is obtained. The excess of acid required can be reduced greatly by carrying out the sulfonation under reduced pressures.[1] Under such conditions, the water of reaction is removed, and the concentration of the sulfonating acid maintained at the desired point. The reaction may be carried out in the apparatus shown in Fig. 2 by delivering benzenesulfonic acid to the jacketed sulfonator and then introducing sulfuric acid at a temperature of 200 to 220°C. to effect disulfonation.

The production of *sulfanilic acid* (1-aminobenzene-4-sulfonic acid) is generally carried out as a two-stage process, but it can also be accomplished directly by the application of partial-pressure distillation. When the former method is used, the sulfuric acid salt is made first, and this is

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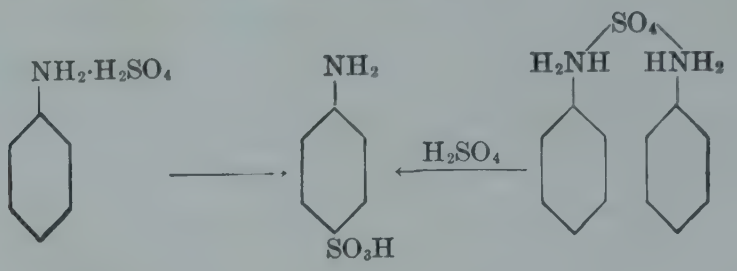
[1] Downs, U. S. 1,279,295 (1918); 1,301,785 (1919).

"baked" at 200°C. *in vacuo* (12 to 15 mm. pressure) to bring about th dehydration and intramolecular rearrangement.

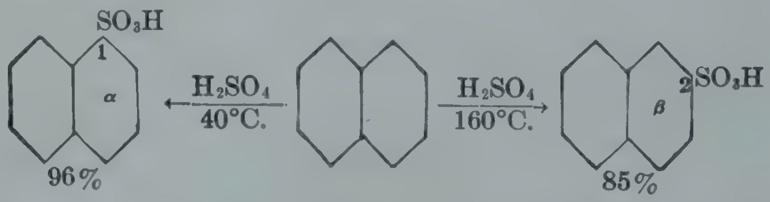


Alternatively, dianiline sulfate may first be prepared by mixing approximately the combining proportions of the materials and then carrying out the sulfonation directly by heating with an excess of strong sulfuric acid.

The isomeric toluidines and xylidines, as well as α-naphthylamine and 1-aminoanthraquinone, can be sulfonated in a similar manner. The —SO_3H group generally enters para to the —NH_2 group, unless this position is occupied.[1] 1-Aminoanthraquinone, however, forms the orthosulfonic acid.

Naphthalenesulfonic Acids.—The sulfonic acids of naphthalene, naphthol, and naphthylamine are numerous and important. In the course of years, these compounds have acquired a wide technical application and are among the most important intermediates in the preparation of azo dyes. The literature pertaining to these compounds is so voluminous and specialized that only a bare outline can be presented here.[2]

In the sulfonation of naphthalene, two isomeric monosulfonic acids are obtained. The proportion of each isomer formed depends on the temperature of sulfonation, but under no conditions is either isomer obtained as the sole product. When the reaction is carried out at 40°C., the α-monosulfonate predominates,



the ratio of the alpha to beta compound being closely 96:4. When sulfonation is effected at 160°C., the beta compound constitutes 85 per cent of the monosulfonic acids formed. The number of isomers that are pos-

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[1] HUBER, *Helvetica Chim. Acta*, **15**, 1372 (1932).

[2] WITT, *Ber.*, **48**, 743 (1915); FIERZ-DAVID, "Grundlegende Operations der Farbenchemie," 1943.

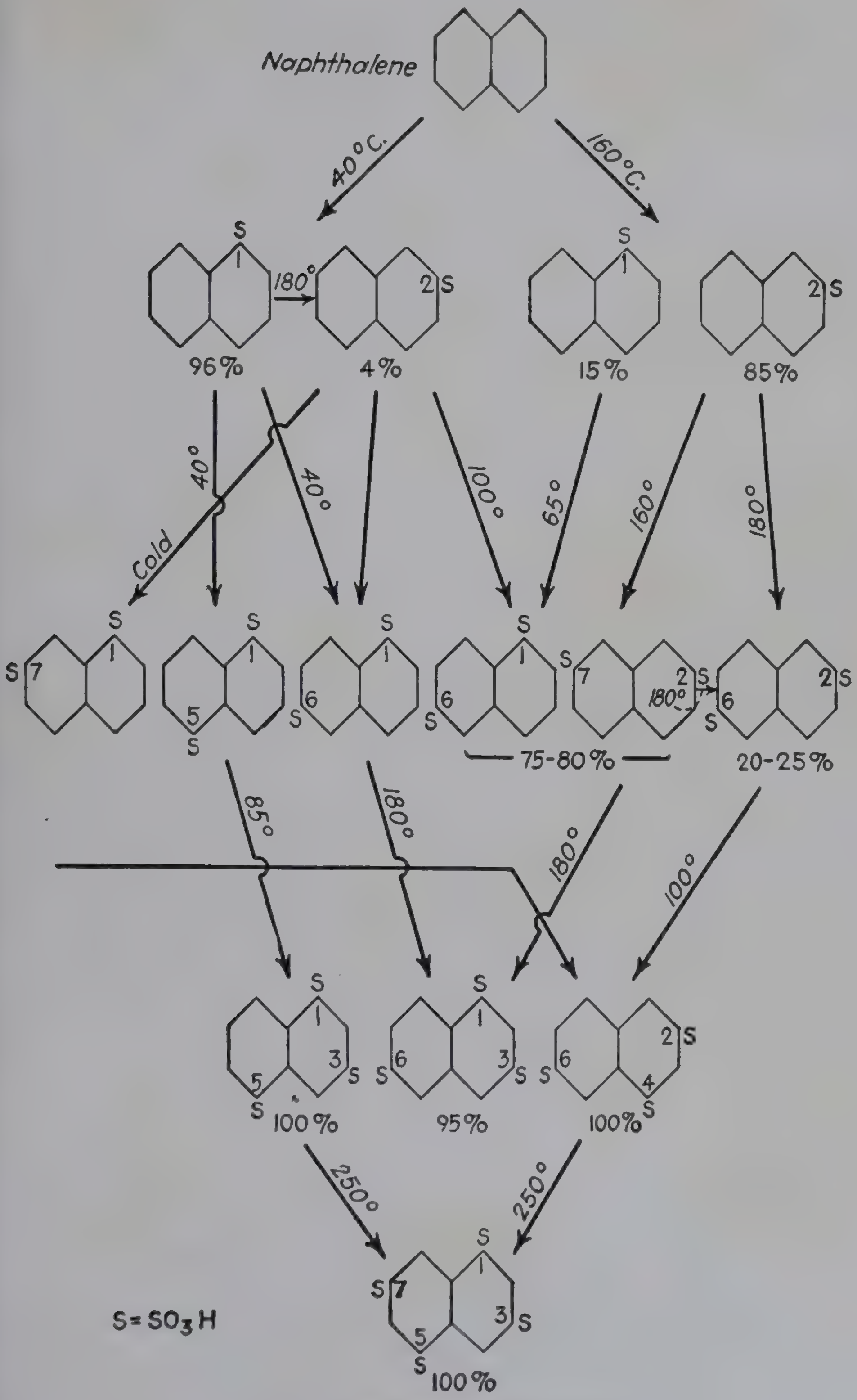

Naphthalene
40°C.
160°C.
S
1
180°
2
S
96%
4%
15%
85%
40°
40°
100°
65°
160°
180°
Cold
S 7 1
1 5 S
6 S 1
6 S 1
S 7 2 S
180°
6 S 2 S
75-80%
20-25%
85°
180°
180°
100°
1 3 S 5 S
100%
6 S 1 3 S
95%
6 S 2 S 4 S
100%
250°
250°
S 7 1 3 S 5 S
100%
S = SO3H

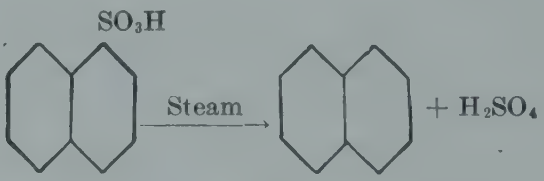
FIG. 3.—Naphthalenesufonic acids.

sible on continued sulfonation is large, and their separation is often very difficult. The isolation of the individual sulfonic acids is the operation that has presented the most interesting and difficult problems in the sulfonation process.

In the further sulfonation of naphthalene, Armstrong and Wynne found that the second —SO_3H group never enters the ortho, para, or peri position to the first.[1] It has also been established that when two sulfonic acid groups are introduced, they enter different nuclei in the naphthalene molecule. At low temperatures, the second sulfo group enters the most remote alpha position and the most remote beta position at high temperatures. Thus, 1-naphthalenesulfonic acid, on further sulfonation in the cold, gives 70 per cent 1, 5-dsiulfonic acid and 25 per cent of the 1, 6-isomer. At higher temperatures, the 1, 6-disulfonic acid is formed predominantly. A schematic representation of the naphthalenesulfonic acids is shown in Fig. 3.

The monosulfonation of naphthalene is practically always carried out with a 25 to 40 per cent excess of sulfuric acid of 93 to 98 per cent strength. In the preparation of the alpha compound, naphthalene is added to the acid below 60°C.; in the production of the beta derivative, the naphthalene is first melted, and the acid run into the melted hydrocarbon at 160 to 165°C. When a sample is distilled with steam and naphthalene is absent, the reaction is considered complete.

In the production of naphthalene-2-sulfonic acid, any unconverted naphthalene along with the 15 per cent of naphthalene-1-sulfonic acid can be removed by passing dry steam into the sulfonation mixture at 150 to 160°C. The alpha compound is desulfonated or hydrolyzed, and the resulting naphthalene is distilled off.



Naphthalene-2-sulfonic acid is almost always converted to the sodium salt, but the methods to this end vary considerably. Frequently, the sulfonation mass is diluted by running into 2 parts of cold water and then neutralizing by addition of dilute hot hydrated lime. The total volume of water added is approximately 5.5 times the original weight of the reactants. The mass is filtered hot, and the calcium naphthalenesulfonates separated from the gypsum. The filtrate is cooled to 30°C., and the calcium sulfonates that separate out are filtered and washed. If the press cake is treated with the calculated amount of soda ash in boiling water, the solution of sodium sulfonates is obtained. This is filtered from the calcium carbonate and allowed to cool. The crystallized

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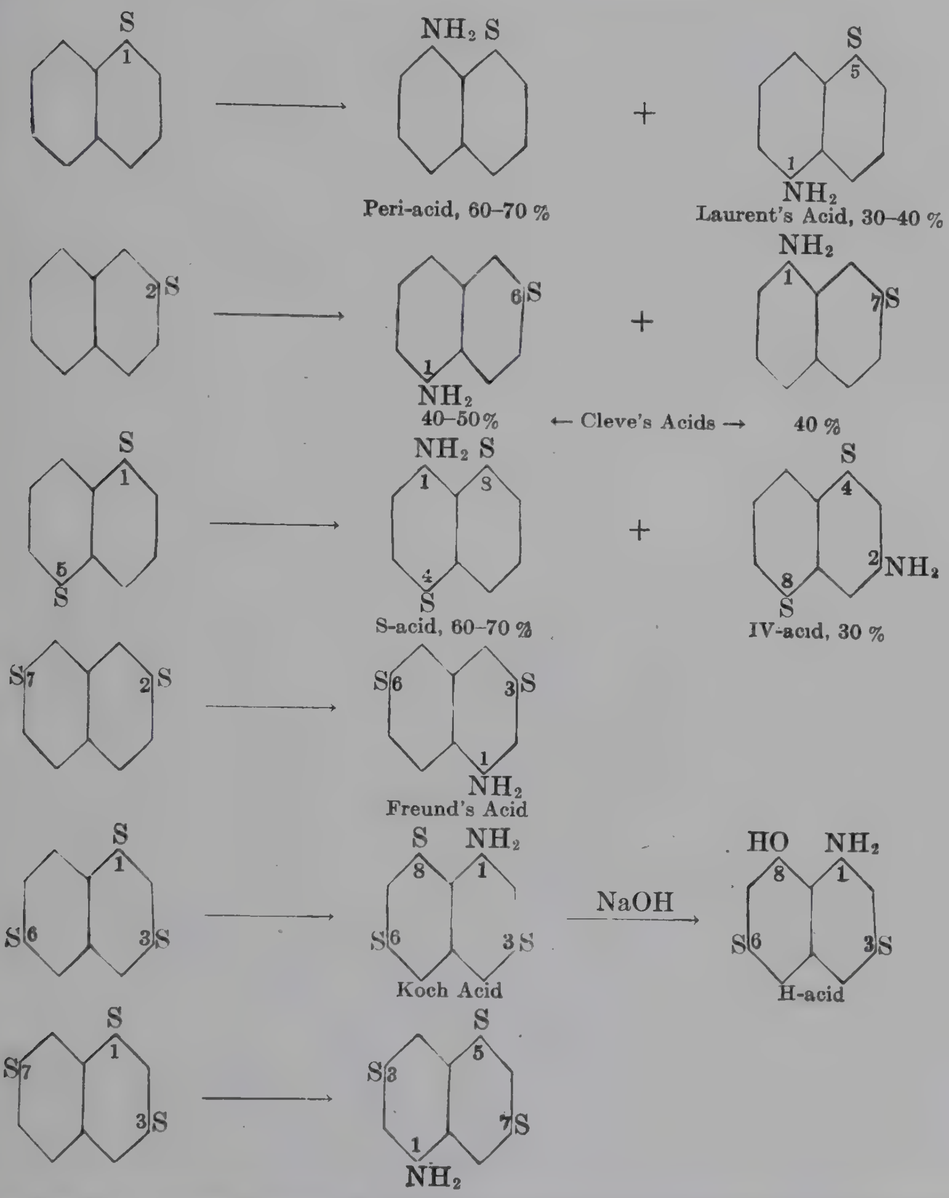
[1] Armstrong and Wynne, *Ber.*, **25**, 226 (1892); **32**, 1136, 3186 (1899); *Ann.*, **361**, 170 (1908).


S
1
NH₂ S
Peri-acid, 60–70 %
S
5
1
NH₂
Laurent's Acid, 30–40 %
2 S
6 S
1
NH₂
40–50 %
← Cleve's Acids →
NH₂
1
7 S
40 %
S
1
5
S
NH₂ S
1
8
4
S
S-acid, 60–70 %
S
4
2 NH₂
8
S
IV-acid, 30 %
S 7
2 S
S 6
3 S
1
NH₂
Freund's Acid
S
1
S 6
3 S
S NH₂
8
1
S 6
3 S
Koch Acid
NaOH
HO NH₂
8
1
S 6
3 S
H-acid
S
1
S 7
3 S
S
5
S 3
7 S
1
NH₂

IG. 4. —Naphthylaminesulfonic acids derived by nitration and reduction of sulfonic acids.

odium naphthalene-2-sulfonate is separated from the mother liquor ontaining the alpha isomer.

The sulfonation mass may also be treated with sodium sulfite conaining some sodium hydroxide and naphthol, which is obtained as a y-product in the subsequent fusion of sodium naphthalene-2-sulfonate. n a further modification, a slight excess over the calculated quantity

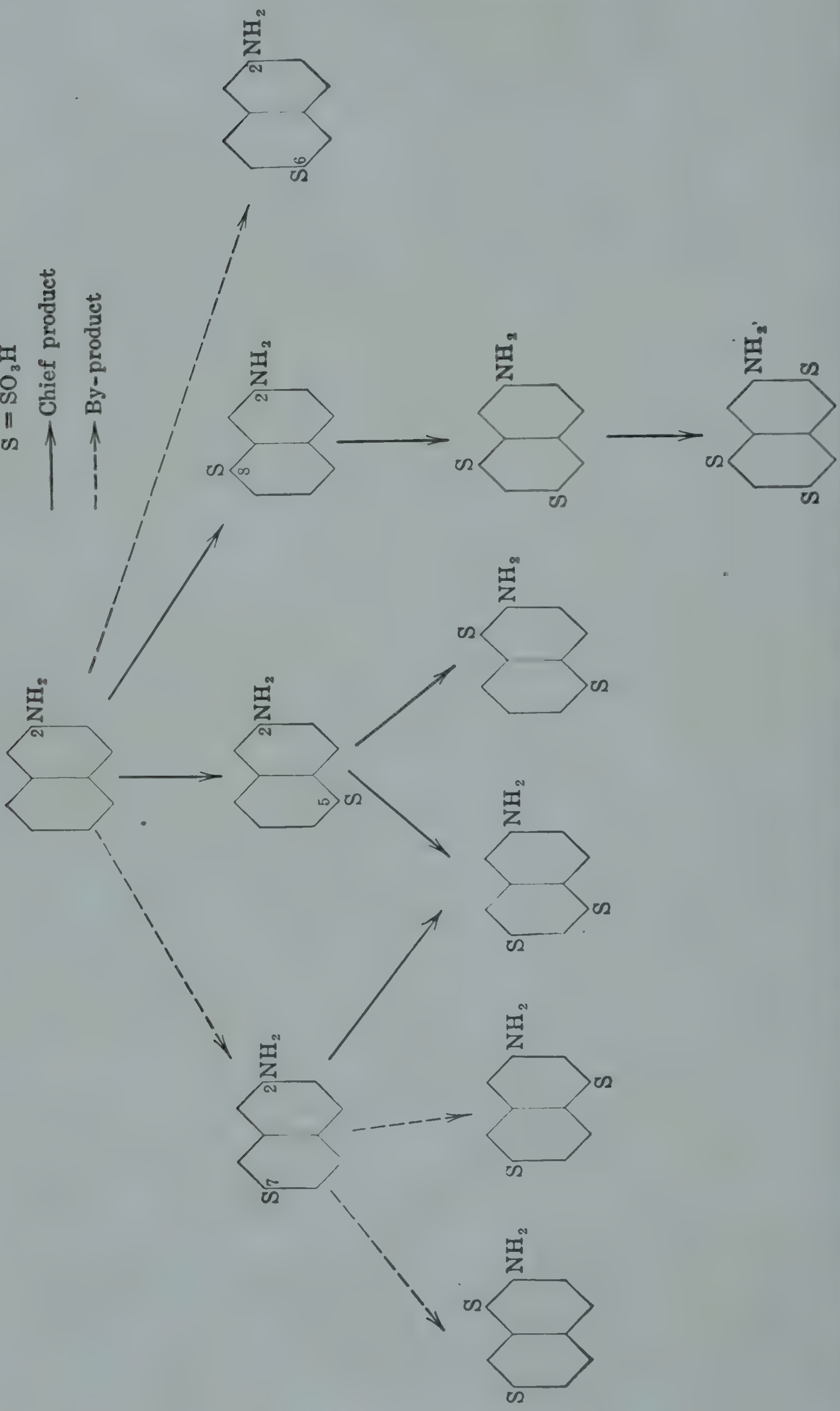

S = SO_3H
Chief product
By-product
NH_2
2
5
6
7
8
S

Fig. 5.—Sulfonic acids derived from β-naphthylamine by sulfonation.

of Glauber's salt is added to the diluted sulfonic acid to form the sodium sulfonate, while the sulfuric acid produced by metathesis is neutralized with lime or chalk. The soluble sodium naphthalene-2-sulfonate is then filtered from the gypsum.

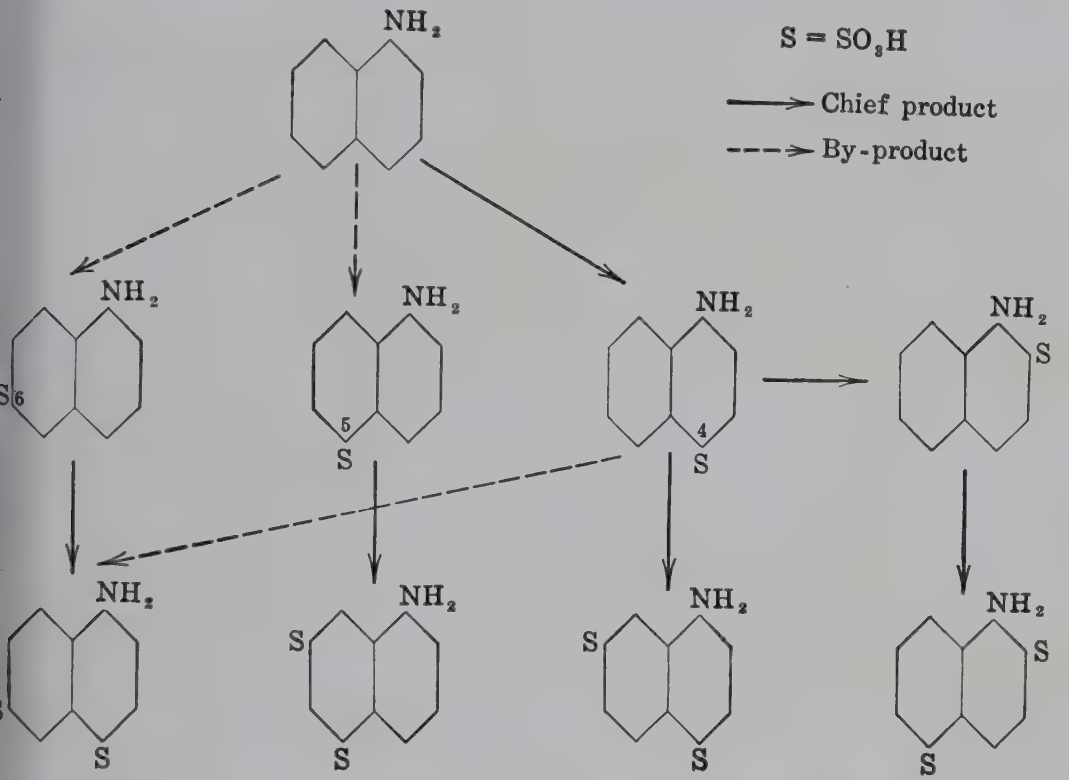
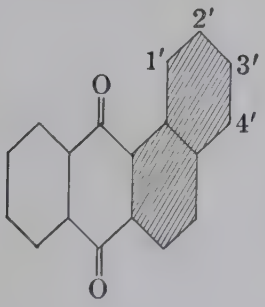

NH₂
S = SO₃H
Chief product
By-product
NH₂
S
6
NH₂
5
S
NH₂
4
S
NH₂
S
NH₂
S
NH₂
S
S
NH₂
S
S
NH₂
S
S

FIG. 6.—Sulfonic acids derived from α-naphthylamine by sulfonation.

In the sulfonation of 1, 2-benzanthraquinone (phthaloyl naphthalene)



y sulfuric acid and oleum, the sulfonic group takes positions analogous o that in the case of naphthalene itself.[1] Thus, 96 per cent sulfuric cid at 150 to 160°C. gives benz 2′-sulfo-1, 2-benzanthraquinone, whereas 0 per cent oleum gives benz 4′-sulfo-1, 2-benzanthraquinone together ith lesser amounts of 2′-isomer.

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[1] Semproni, *Gazz. chim. ital.*, **69**, 448 (1939).

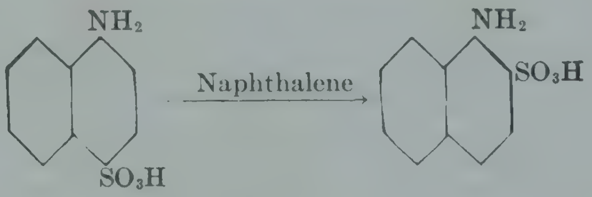
Naphthylaminesulfonic Acids.—Of greater technical importance than the naphthalenesulfonic acids are the naphthylaminesulfonic acids These compounds are derived by three general methods:

1. Nitrating a sulfonic acid and then reducing. The products obtained by this procedure are set forth in Fig. 4.
2. Sulfonating a nitro compound and then reducing.
3. Sulfonating an amino compound, which leads to the naphthylamine sulfonic acids shown in Figs. 5 and 6.

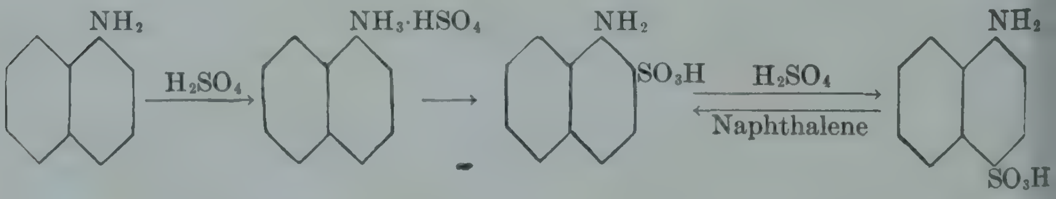
Naphthionic acid, 1-aminonaphthalene-4sulfonic acid is prepared from α-naphthylamine by the baking process (see Sulfanilic Acid, pages 322–323).

After the sulfate of the amine is heated in a vacuum oven for 8 hr. at 180°, the unconverted naphthylamine (5 to 10 per cent) is recovered from the sodium sulfonate solution by benzene extraction. As indicated in Fig. 6, some 1, 5-acid (Laurent's acid) accompanies the naphthionic acid. To remove this impurity, the solution of sodium naphthionate is concentrated and then cooled to effect the crystallization of the principal product.

1-*Naphthylamine*-2-*sulfonic acid* is prepared by heating the dried sodium naphthionate obtained from the previous operations with 2 to 3 parts of naphthalene at 217°C., the conversion taking place in 3 hr. The excess of naphthalene is recovered by adding water to the cooled charge and blowing steam through the reaction mass.

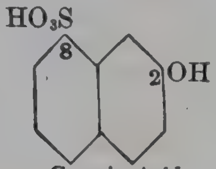


This reaction is of interest in showing the influence of an excess of naphthalene or sulfuric acid on the migration of the sulfonic acid group. The course of the reaction is probably as follows:

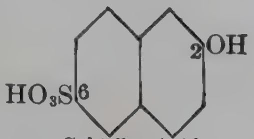


In the monosulfonation of β-naphthol leading to the formation of Crocein and Schäffer acids (see below), there is a similar migration of the sulfonic acid group to the most stable positions in the presence of an excess of sulfuric acid and at comparatively high temperatures.

2-Naphtholsulfonic Acids.—When β-naphthol is sulfonated with approximately 2 parts of sulfuric acid (93 per cent), a mixture of two monosulfonic acids is obtained, *viz.*, Crocein acid and Schäffer acid.



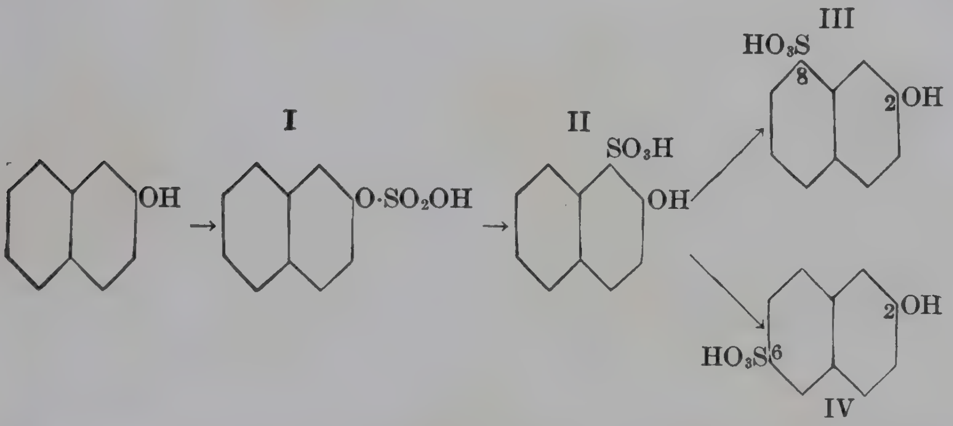
Crocein Acid



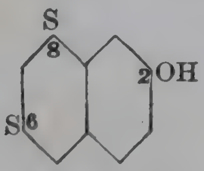
Schäffer Acid

At low temperatures, *i.e.*, 20°C., the former predominates; but at higher temperatures (100 to 110°C.), the latter is the principal product.

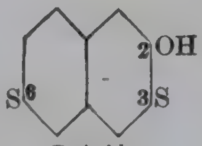
It is known that the initial product of reaction is the 2-naphthol-1-sulfonic acid II presumably derived from the sulfuric acid ester I at 20 to 40°C. and transformed to the isomeric Crocein acid III at slightly higher temperatures. The most stable of the monosulfonic acids, obtained either by the direct sulfonation of β-naphthol at 100°C. or by further heating of Crocein acid, is 2-naphthol-6-sulfonic acid (Schäffer acid).



When the quantity of sulfuric acid is increased, two disulfonic acids are formed, the proportion of each isomer again depending on the sulfonation temperature employed. When operations are carried on at 30 to 35°C., G acid (2-naphthol-6, 8-disulfonic acid) predominates; and, at 60°C., R acid (2-naphthol-3, 6-disulfonic acid) is the principal product.



G Acid



R Acid

Naphtholsulfonic acids may also be obtained by the alkali fusion of naphthalenedisulfonic acids. Thus, 2-naphthol-7-sulfonic acid (F acid) is obtained by causticizing naphthalene-2, 7-disulfonic acid. Only one sulfonic acid group is attacked by proper regulation of the fusion temperature and the proportions of the reactants.

Similarly, Gamma acid, *i.e.*, 2-amino-8-naphthol-6-sulfonic acid (Fig 7), is preferably made by the disulfonation of β-naphthylamine to 2-naphthylamine-6, 8-disulfonic acid (amino G acid) which is then treated in an autoclave with caustic soda and nitrite solution.

Some of the important amino derivatives obtained from 2-naphtholsulfonic acids by ammonolysis according to the Bucherer reaction are shown in Fig. 7.

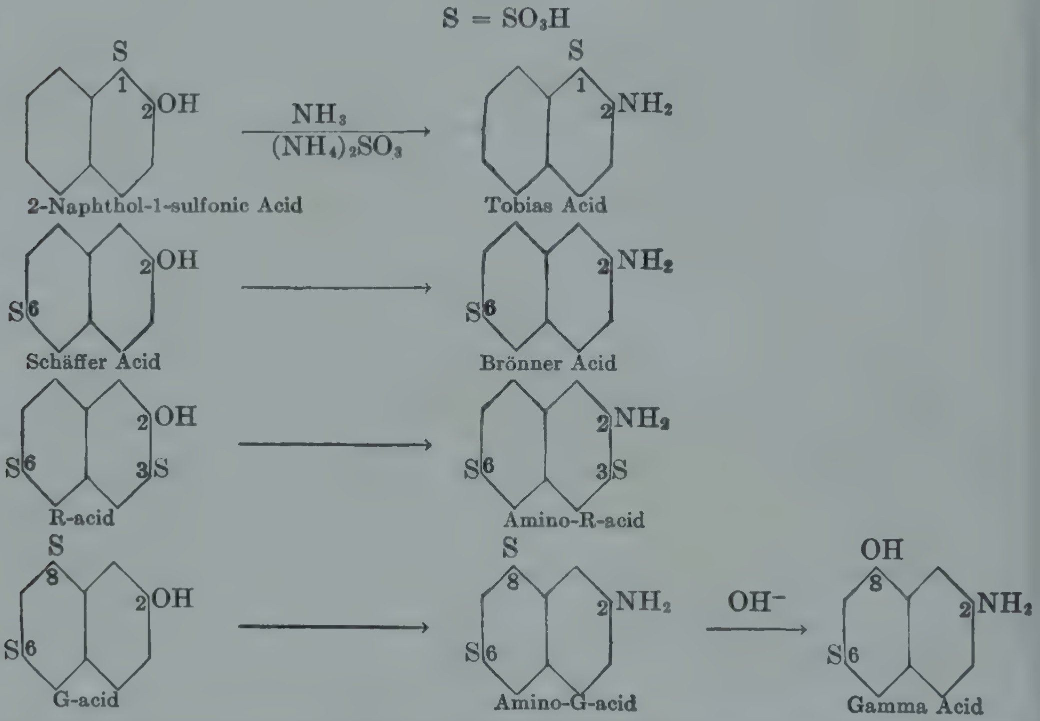


Fig. 7. Amino derivatives obtained from 2-naphtholsulfonic acids by Bucherer reaction.

Oleum as a Sulfonating Agent

Introduction.—It has been pointed out that sulfuric acid comprises a series of hydrates of sulfur trioxide, some of which are very unstable,[1] and experience has shown that the activity of sulfuric acid as a sulfonating agent is directly related to its SO_3 concentration.

From our present knowledge of the sulfonation process, it appears that aqueous sulfuric acid may be conceived as a solvent for the active sulfonating agent, *viz.*, free or combined sulfur trioxide. Water does, of course, ameliorate the intensity of the reaction and, in many sulfonations, inhibits the formation of oxidation products and to that extent performs a beneficial service. Current developments indicate that sulfur

[1] Baumgarten, *Ber.*, **64B**, 1502 (1931).

trioxide alone or as 40 to 50 per cent oleum[1] is being advantageously employed to obviate the decelerating influence of water.[2] A number of simple expedients are being employed, *e.g.*, (1) adding oleum to the reaction mass comprising all the organic compound dissolved or suspended in cycle sulfuric acid, *i.e.*, spent acid from previous operations; (2) adding oleum and organic compound concurrently to a large mass of reacting material at equilibrium insofar as sulfonation is concerned; and (3) using part of the residual acid from disulfonation to effect monosulfonation and then introducing oleum for the disulfonation step. Such procedures make possible the presence of only a small excess of SO_3 at any stage of the reaction and thus inhibit the tendency to disulfonation and are also conducive to economies in the amount of SO_3 that must be employed.

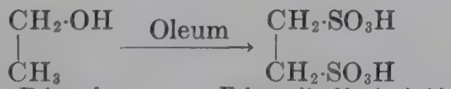
When water or sulfuric acid is the solvent, the organic compound will remove the combined SO_3 until a point is reached when the affinity of SO_3 for $(H_2O)_x$ under the conditions of operation is equal to that of SO_3 for the organic compound. An equilibrium then exists. Naphthalene, which readily forms addition compounds with SO_3, is sulfonated at comparatively low temperatures with comparatively weak acids. Benzene, however, requires a more concentrated acid; for when the hydrate $SO_3{\cdot}3H_2O$ corresponding to 73 per cent H_2SO_4 is formed, it will no longer give up SO_3 to benzene to form the sulfonic acid.

Oleum (100 per cent sulfuric acid containing dissolved sulfur trioxide) is used instead of sulfuric acid for sulfonation in cases where the reaction proceeds with difficulty even with the application of heat. It finds extensive use in the preparation of polysulfonic acids, the formation of which necessitates the presence of either free SO_3 or minimal quantities of water. The reaction for monosulfonation is as follows:

$$R{\cdot}H + SO_3 \rightarrow R{\cdot}SO_2{\cdot}OH$$

No water is produced; the free SO_3 concentration of the sulfuric acid merely decreases; for this reason, its use is often more economical than that of sulfuric acid.

Treatment of Aliphatic Compounds with Oleum.—Whereas methane is not attacked by oleum, all its homologues beginning with hexane can be sulfonated. Oleum reacts with ethanol and with ether to form ethanedisulfonate.



$$\begin{array}{c} CH_2{\cdot}OH \\ | \\ CH_3 \end{array} \xrightarrow{\text{Oleum}} \begin{array}{c} CH_2{\cdot}SO_3H \\ | \\ CH_2{\cdot}SO_3H \end{array}$$

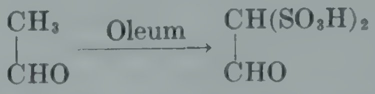
Ethanol Ethanedisulfonic Acid

---

[1] Percentage of oleum = (% total H_2SO_4 − 100) × (80 ÷ 18).

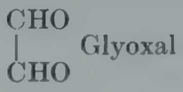
[2] This trend was predicted in the first edition.

Aliphatic aldehydes and ketones yield di- and trisulfonic acids when treated with oleum. The reaction with acetaldehyde may be represented as follows:



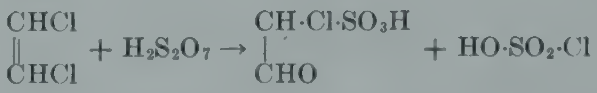
$$\begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \xrightarrow{\text{Oleum}} \begin{matrix} CH(SO_3H)_2 \\ | \\ CHO \end{matrix}$$

The sulfonic acid thus formed may be considered as being a derivative of glyoxal.



$$\begin{matrix} CHO \\ | \\ CHO \end{matrix} \quad \text{Glyoxal}$$

Acetone, when treated with 65 per cent oleum at moderate temperatures, gives acetone trisulfonic acid in good yield. Also if certain unsaturated aliphatic halides are treated with oleum, halogeno sulfo aldehydes are obtained. Thus:[1]



$$\begin{matrix} CHCl \\ \| \\ CHCl \end{matrix} + H_2S_2O_7 \rightarrow \begin{matrix} CH{\cdot}Cl{\cdot}SO_3H \\ | \\ CHO \end{matrix} + HO{\cdot}SO_2{\cdot}Cl$$

Treatment of Aromatic Compounds with Oleum.—The use of oleum for the sulfonation of nitrobenzene typifies its use in the aromatic series. In this instance, nitrobenzene is not appreciably sulfonated by sulfuric acid, and the use of oleum is therefore a necessity. In other cases, where it is desired to prepare polysulfonic acids, the entrance of the first sulfonic group may be effected by means of sulfuric acid, further sulfonation being conditioned on the introduction of oleum. The preparation of naphthalenetrisulfonic and anthraquinonedisulfonic acids is an example of such usage.

The dependence of velocity of sulfonation on the SO_3 concentration is brought out in a striking manner in the treatment of *p*-nitrotoluene with sulfuric acid and oleum. The introduction of only slight amounts of water greatly retards the reaction rate, particularly when the sulfonating acid is weaker than 100 per cent H_2SO_4. At 25°C., the velocity coefficients (in reciprical minutes) are[2]

In oleum, 2.4 % SO_3	0.003
In 100 % H_2SO_4	0.0004
In 99.4 % H_2SO_4	0.0000005

The velocity increases 2 to 2.5 times for each rise of 10°C. in temperature.

The trisulfonation of naphthalene incident to the preparation of Koch acid (1-aminonaphthalene-3, 6, 8-trisulfonic acid) provides an example illustrating the use of concentrated sulfuric acid for effecting monosulfonation, this step then being followed by the introduction of oleum to ensure the formation of the trisulfonic acid. The reactions involved may be represented as follows:

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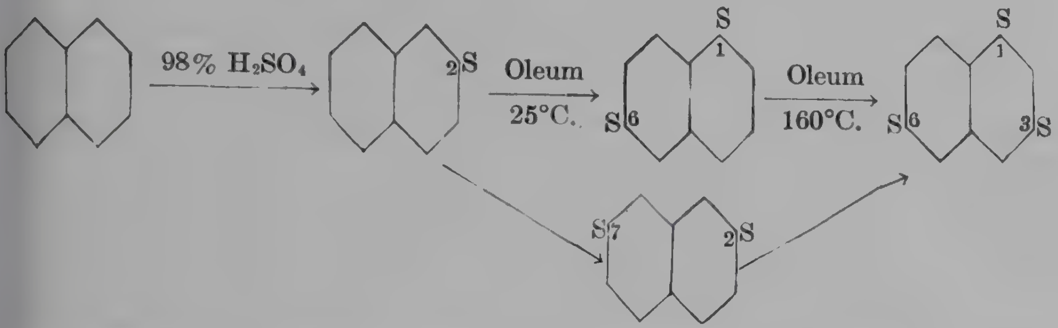
[1] Ger. 362,744 (C. 1923 II 1246).

[2] MARTINSEN, *Z. physik. Chem.*, **62**, 713 (1908).



Sulfonation of Anthraquinone. General Remarks.—Of the numerous anthraquinonesulfonic acids theoretically possible, only two mono acids and six disulfonic acids are known.

In general, they are prepared by the action of oleum on anthraquinone, although anthraquinonesulfonic acids may be made from α-nitro derivatives by replacing the —NO_2 by —SO_3H, by oxidizing anthracenesulfonic acids, by the oxidation of anthraquinone mercaptans, and by the action of sodium sulfite on halogen derivatives of anthraquinone.

The behavior of anthraquinone on direct sulfonation is simpler than the corresponding naphthalene chemistry. Unlike the latter, acid concentration and time and temperature of reaction determine only the degree of sulfonation and not the orientation—which is influenced only by the presence or absence of a catalyst. As in the case of naphthalene, the monosulfonation of anthraquinone does not result in a uniform product—more or less disulfonic acids always being present, the quantity being dependent on the conditions employed. The monosulfonic acid formed appears to undergo sulfonation just as readily as does anthraquinone, resulting in an equilibrium between the anthraquinone mono- and disulfonic acids. Because of the easy formation of disulfonic acids in monosulfonation, an excess of anthraquinone is employed; or in other words, the quantity of SO_3 used is sufficient to convert only part (50 per cent) of the anthraquinone. In the absence of a catalyst, the sulfonic acid groups enter almost exclusively in beta positions. When a mercury catalyst is employed, alpha substitution takes place.

Anthraquinone-β-sulfonic Acids.—The sulfonation of anthraquinone to form the β-monosulfonic acid can be accomplished by employing 2.5 parts of concentrated sulfuric acid and heating at 250 to 260°C. The reaction can be carried out more readily, however, by using oleum at 120 to 140°C. The production of disulfonic acids (Fig. 8) approximately parallels the formation of the monosulfonic acid, the relative quantities of each being dependent principally on the SO_3 ratio and the temperature

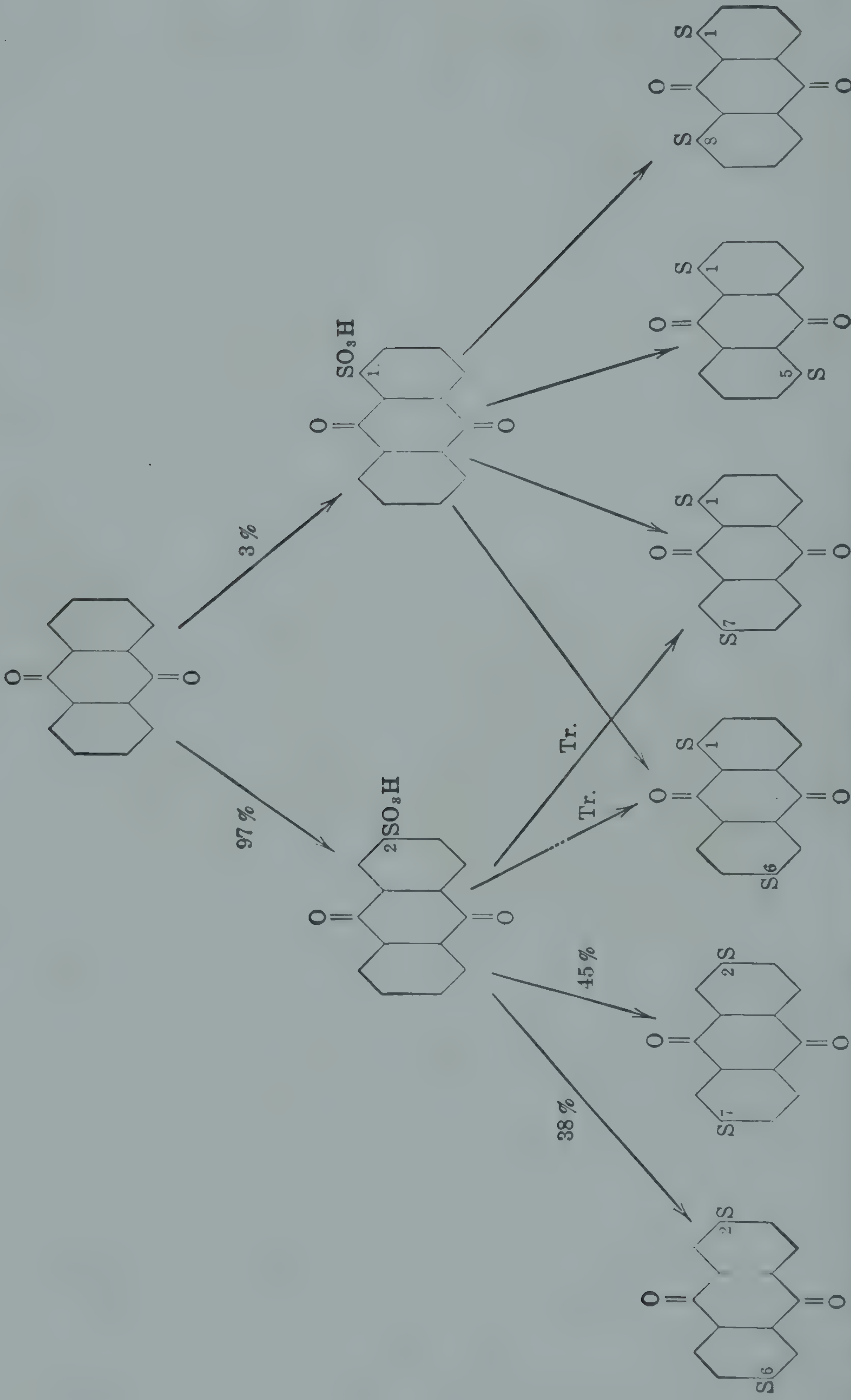
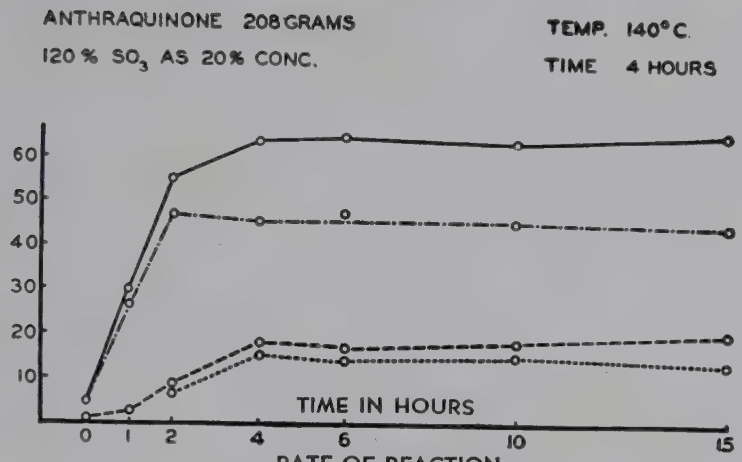
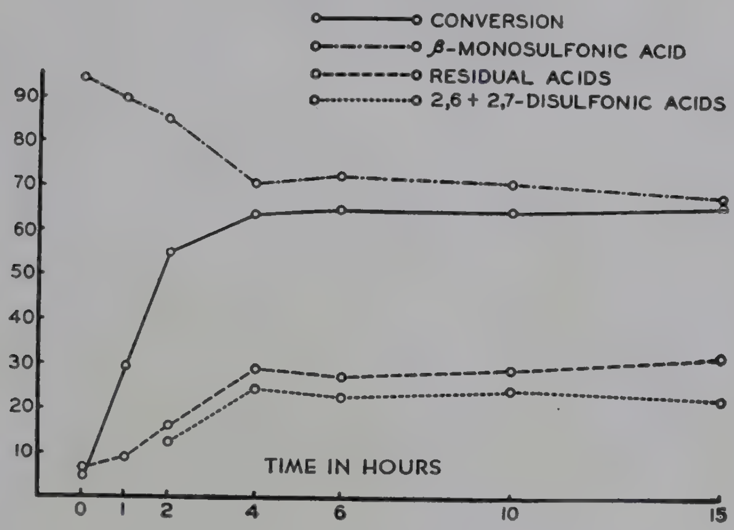

3 %
97 %
SO₃H
SO₃H
Tr.
Tr.
45 %
38 %

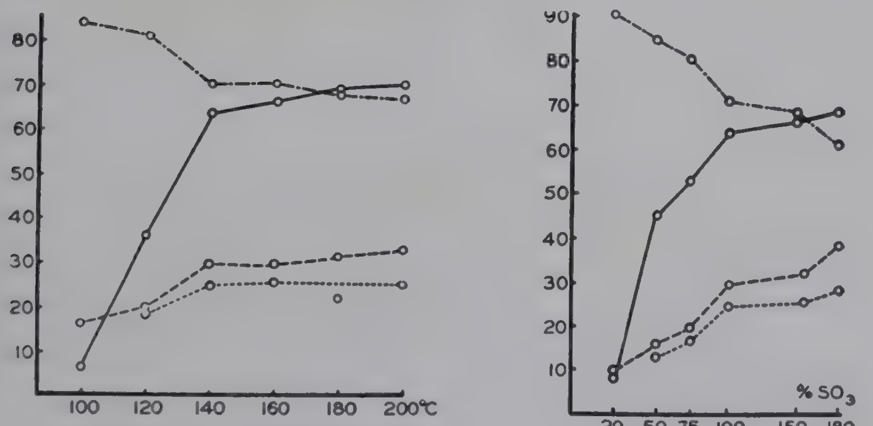
FIG. 8.—Noncatalytic sulfonation of anthraquinone.



RATE OF REACTION



RATIO OF SULFONIC ACIDS



EFFECT OF TEMPERATURE

EFFECT OF SO_3 RATIO

FIG. 9.—Factors: preparation of anthraquinone-2-sulfonic acid. Each of the charts above contains one variable. Per cent yield is plotted against variable.

and time of reaction. To avoid excessive disulfonation, it is customary to use only about 70 per cent of the quantity of free SO_3 required by theory. Under such conditions, about 50 per cent of the anthraquinone treated remains unconverted (Table I), and about 16 per cent of the converted material is found as the 2, 6- and 2, 7-anthraquinonedisulfonic acids.[1] About 5 per cent of other acids are formed simultaneously, and these include 2 to 3 per cent of the α-monosulfonic acid, the rest being hydroxysulfonic acids.

Disulfonation ceases when the SO_3 concentration of the sulfonating acid drops to 2 per cent, for the monosulfonic acid remains unaltered when treated with 2 per cent oleum at 140°C. The isomeric 2, 6- and 2, 7-anthraquinonedisulfonic acids are formed in practically the same quantities. The curves in Fig. 9 show the effect of various factors in the preparation of anthraquinone-2-sulfonic acid. When anthraquinone is completely sulfonated with 120 per cent of the theoretical quantity of 40 per cent oleum, the results shown in the curves of Fig. 10 are obtained.[2] Sulfonation at 190°C. with 40 per cent oleum (110 per cent of theory) results in a yield of 85 per cent 2, 6- and 2- 7-anthraquinonedisulfonic acids, the ratio of the isomers being 1:1.15. As the temperature of sulfonation is lowered, the relative proportion of the 2, 7-disulfonic acid increases.

TABLE I.—SULFONATION OF ANTHRAQUINONE[1]
Effect of SO_3 Ratio
Anthraquinone, 104 Gm.; Oleum, 20 Per Cent SO_3; Temperature, 140°C.; Reaction Time, 4 Hr.

% of theory, SO_3	Unconverted anthraquinone		Conversion	Sodium salt		2, 6-Salt (Na)		2, 7-Salt (Na)		Residual acids
	Grams	%	%	Grams	% of conversion	Grams	%	Grams	%	%
20	95.5	91.9	8.1	11.5	90.8	....	....	....	....	9.2
50	57.1	55.0	45.0	58.9	84.3	5.6	6.1	6.0	6.5	3.1
75	49.1	47.3	52.7	66.2	80.4	8.7	8.0	9.2	8.5	3.1
75	50.1	48.1	51.9	64.1	79.8	7.9	7.4	8.5	8.0	4.8
100	38.5	37.0	63.0	69.3	70.9	13.4	10.3	14.1	10.9	7.9
150	35.4	34.1	65.9	69.4	67.9	16.3	12.0	17.7	13.1	7.0
150	35.2	33.8	66.2	68.7	67.0	15.5	11.4	16.9	12.4	9.2
180	32.7	31.5	68.5	65.6	61.7	19.4	13.8	20.0	14.2	10.3
180	31.3	30.1	69.9	65.3	60.3	19.3	13.4	20.1	13.9	12.4

[1] LAUER, *J. prakt. Chem.*, **130** (1931).

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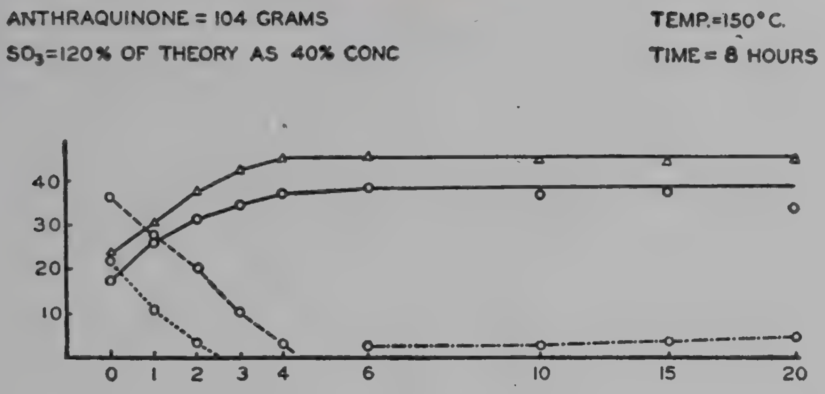
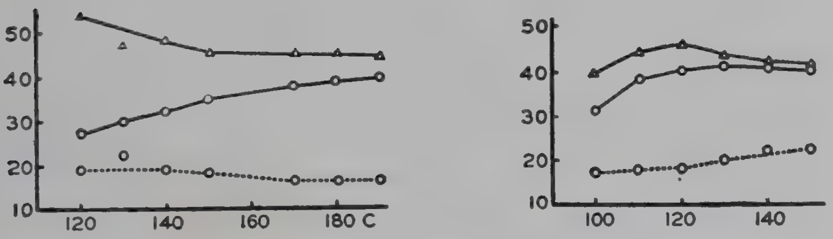
[1] LAUER, *J. prakt. Chem.*, **130,** 198 (1931).

[2] LAUER, *loc. cit.*

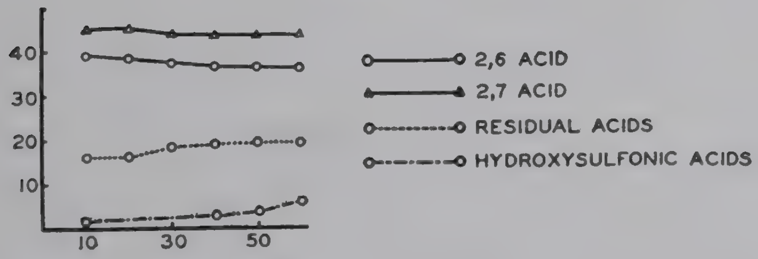


EFFECT OF TIME



EFFECT OF TEMPERATURE

EFFECT OF SO_3 RATIO



EFFECT OF SO_3 CONC.

Fig. 10.—Factors: preparation of anthraquinone-β, β-disulfonic acids. Each of the charts above contains one variable. Per cent yield is plotted against variable.

In addition to the two principal easily isolatable disulfonic acids, there are also present in the mother liquor (1) hydroxysulfonic acids, 3 per cent; (2) α, β-disulfonic acids, 3 per cent; (3) β, β-disulfonic acids, 10 per cent.

Anthraquinone-1-sulfonic Acid.—The sulfonation of anthraquinone in the presence of mercury or a mercury salt causes substitution to take place almost exclusively in alpha positions.

Catalytic Sulfonation of Anthraquinone.—Approximately 1 per cent by weight of mercury to anthraquinone used is required if 20 to 30 per cent oleum is used. An increase in the concentration of the catalyst above this ratio does not, as can be seen from the data in Table II, appreciably alter the character of the results. When the strength of the oleum is reduced from 20 to 5 per cent SO_3, an increased proportion of the catalyst displays a definite hindrance to the formation of beta sulfonic acids. The data in Table V (page 306) show that the mercury salt anion is without effect, since any of the salts give similar results.

TABLE II.—PREPARATION OF ANTHRAQUINONE-1-SULFONIC ACID*
Effect of Catalyst Ratio
Anthraquinone, 104 Gm.; SO_3, 100 Per Cent of Theory; Time of Reaction, 3 Hr.; Temperature, 140°C.

Strength of oleum, % SO_3	Volume, cc.	Hg, %	Alpha acids, %	Beta acids, %
20	110	1.0	92.8	7.2
20	110	2.0	91.3	8.7
20	110	3.0	92.1	7.9
10	220	1.0	90.8	9.2
10	220	2.0	93.1	6.9
10	220	3.0	93.7	6.3
5	440	1.0	91.6	8.4
5	440	2.0	94.0	6.0
5	440	3.0	95 4	4.6
5	440	4.0	98.3	1.7
5	440	4.5	98.7	1.3
5	440	5.0	99.1	0.9

* LAUER, *J. prakt. Chem.*, **135**, 174 (1932).

The curves in Fig. 11 show the effect of various factors in the preparation of anthraquinone-1-sulfonic acid. Here the acid was precipitated as the potassium salt, a second fraction being obtained from the first filtrate.

Goldberg has shown that the orienting influence of mercury applies also to the sulfonation of alpha and beta chloroanthraquinones.[1] This procedure provides a new means of obtaining di- and trichloroanthraquinones.

---

[1] GOLDBERG, *J. Chem. Soc.*, **1931**, Pt. 2, 1777.

α-Anthraquinonedisulfonic Acids.—The principal products obtained by the catalytic disulfonation of anthraquinone are the 1, 5- and 1, 8-acids. According to Krebser, these are formed to the extent of 45 to 50 per cent and 27 per cent, respectively.[1]

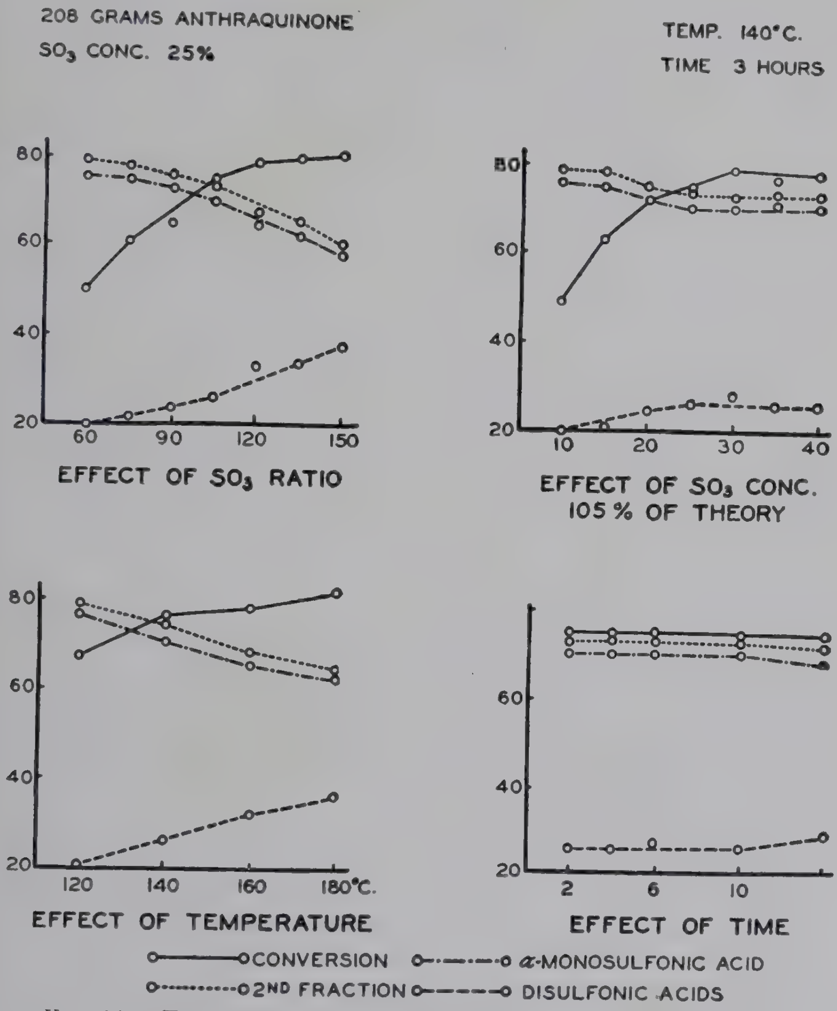
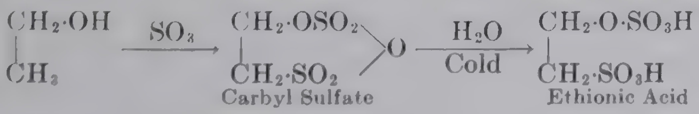


Fig. 11.—Factors: preparation of anthraquinone-1-sulfonic acid. Each of the charts contains only one variable. Per cent yield is plotted against variable.

Sulfonation with SO_3 Alone

Sulfur trioxide finds use in the sulfonation of both aliphatic and aromatic compounds.

The reaction of sulfur trioxide with absolute ethanol results in the formation of carbyl sulfate,



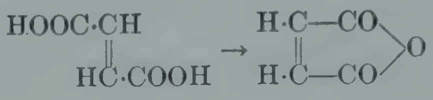
$$\begin{array}{l}CH_2{\cdot}OH\\ |\\ CH_3\end{array} \xrightarrow{SO_3} \begin{array}{l}CH_2{\cdot}OSO_2\\ |\\ CH_2{\cdot}SO_2\end{array}\!\!>O \xrightarrow[\text{Cold}]{H_2O} \begin{array}{l}CH_2{\cdot}O{\cdot}SO_3H\\ |\\ CH_2{\cdot}SO_3H\end{array}$$

---

[1] Krebser, Diss. E. T. H., Zurich (1925).

which, on hydrolysis in the cold, yields ethionic acid. The constitution of this acid indicates it to be both a sulfonic acid and a sulfuric acid ester. This observation appears correct, since carbyl sulfate is converted to isethionic acid ($HO \cdot CH_2 \cdot CH_2 \cdot SO_3H$)[1] upon warming with water.

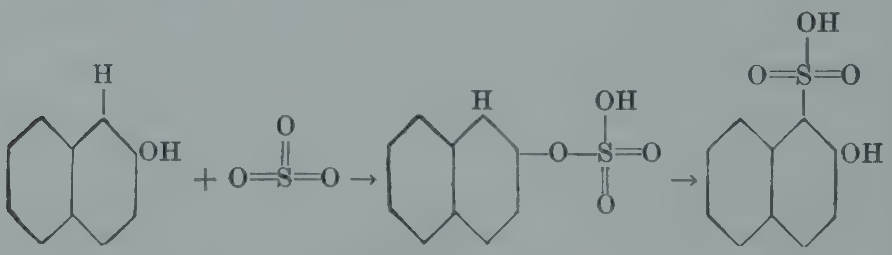
On sulfonating fumaric acid with SO_3, maleic anhydride is formed first, rearrangement and dehydration taking place, thus:



When 3 moles of SO_3 per mole of maleic or fumaric acids is employed at 60 or 70°C., respectively, a yield of 87 per cent of sulfomaleic acid as $(C_4HO_7S)_2Ba_3$ is obtained.[2]

In the aromatic series, sulfur trioxide has been used for the sulfonation of *p*-dichlorobenzene and *m*-chlorobenzoic acid,[3] gaseous SO_3 being passed directly into the melted substances.

A comparatively inert solvent may be employed for the sulfonation of compounds that react readily with sulfur trioxide. When β-naphthol is suspended in nitrobenzene containing SO_3 at 16°C., 2-naphthol-1-sulfonic acid is obtained. Tetrachlorethane ($C_2H_2Cl_4$) is used[4] as a solvent in the sulfonation of amines such as *m*-xylidine, and β-naphthylamine with sulfur trioxide. This method is employed advantageously when the ortho sulfonic acid is desired instead of the para isomer. The mechanism of addition and intramolecular rearrangement with respect to the preparation of 2-naphthol-1-sulfonic acid (and 2-naphthylamine-1-sulfonic acid) is probably as follows:



Lauer has found that the presence of water plays an important role in the orientation of the sulfonic acid group.[5] The substituents already present have only a limited directing influence when H_2SO_4 is the sulfonating agent and exclusively meta or ortho-para acids are not usually obtained. When, however, SO_3 is used, either as a gas or in the presence of an organic solvent, and the reactants are free of moisture, only ortho-para or only meta compounds are formed, as is evident from the data in Table III. What appears as an exception to this rule is the sulfonation of toluene with SO_3, but this can be explained by the presence of water in the reaction mass as a result of sulfone formation, thus:

---

[1] This is converted to taurine ($H_2N \cdot CH_2 \cdot CH_2 \cdot SO_3H$) by ammonolysis.

[2] Backer and Zanden, *Rec. trav. chim.*, **49**, 735 (1930).

[3] Otto, *Ann.*, **123**, 216 (1862).

[4] U. S. 1,794,861 (1931).

[5] Lauer, *J. prakt. chem.*, **143**, 127 (1935).

$$2C_6H_5CH_3 + SO_3 \rightarrow (C_6H_4CH_3)_2SO_2 + H_2O$$

When this reaction is carried out in the presence of acetic anhydride or phosphorus pentoxide, only ortho and para sulfonic acids are obtained.

Table III.—Influence of Substituents, Sulfonation of Benzenoid Compounds

Substituent	With H_2SO_4			With SO_3		
	% composition			% composition		
	Ortho	Para	Meta	Ortho	Para	Meta
NO_2	..	3	97	..	...	100
SO_3H	..	5	95	..	...	100
CHO	..	...	100	..	...	100
COOH	..	14	86	..	...	100
CO	..	...	100			
CCl_3	..	...	...	..	...	100
$CHCl_2$	10	60	30			
CH_3	15	80	5	20	80	
Br	4	96	...	..	100	
I	2	98	...	..	100	
Cl	..	100	...	..	100	
NHAc	..	100				
OH	15	85				

Sulfur Dioxide as Solvent.—Sulfur trioxide dissolved in liquid SO_2 can be used to advantage in effecting many difficult sulfonations and is particularly useful in the preparation of sulfoarylalkanes which are important detergents. This technic has the advantage over ordinary sulfonation processes in that it can be controlled at low temperatures (about 5°) by permitting vaporization of some of the solvent to remove the heat of reaction. The formation of undesirable charred and oxidation products is thus avoided. Liquid SO_2 is also employed as the solvent in the sulfonation of stearic acid with SO_3.[1] Upon removal of the bulk of sulfur dioxide, an alpha sulfonic acid derivative of stearic acid is obtained which is converted to the ammonium salt by treatment with gaseous ammonia.

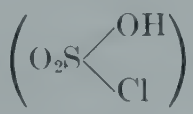
[1] Datin and Bardwell, U. S. 2,324,199 (1943).

Sulfonation with Acid Sulfates

Bisulfates, *e.g.*, $NaHSO_4$, and trihydrosulfates, *e.g.*, $NaHSO_4{\cdot}H_2SO_4$, of the alkali metals may be employed as sulfonating agents, but their use is distinctly limited. The activity of the acid sulfates may be considered as a modification of the action of concentrated sulfuric acid, since the salts contain no water. The trihydrosulfate $KH_3(SO_4)_2$ melts at approximately 100°C. and can therefore be used more advantageously than the acid sulfate $KHSO_4$, which melts at 210°C. When the acid sulfates are obtained as by-products from the manufacture of nitric acid, they may be employed to advantage in the preparation of 1-aminoanthraquinone-2-sulfonic acid. Here the reaction is carried out by treating 1-aminoanthraquinone at 210 to 240°C. under reduced pressure.[1]

Benzene, toluene, and naphthalene are sulfonated only with indifferent success by trihydrosulfates. Using 2 parts of $NaH_3(SO_4)_2$ per part of benzenesulfonic acid and heating at 240°C. Gebler obtained the disodium salt of benzene-1, 3-disulfonic acid with practically quantitative yields.[2] Naphthalene is converted to sodium β-naphthalenesulfonate when similarly treated at 180°C. for 8 hr.

Chlorosulfonic Acid $\left(O_2S\begin{matrix}OH\\Cl\end{matrix}\right)$ as a Sulfonating Agent



Chlorosulfonic acid reacts with hydrocarbons, both aliphatic and aromatic, and the reaction may be represented by the following equations:

$$R{\cdot}H + Cl{\cdot}SO_2{\cdot}OH \rightarrow R{\cdot}SO_2{\cdot}OH + HCl$$
$$R{\cdot}SO_2{\cdot}OH + Cl{\cdot}SO_2{\cdot}OH \rightarrow R{\cdot}SO_2{\cdot}Cl + H_2SO_4$$

The first reaction results in the formation of the sulfonic acid of the hydrocarbon and hydrogen chloride; the second produces the sulfonylchloride of the hydrocarbon and sulfuric acid. The ordinary method of carrying out the first reaction is to dissolve or suspend the hydrocarbon in an inert solvent, such as CS_2, $CHCl_3$, or CCl_4, and to add the required quantity of chlorosulfonic acid gradually, heating if necessary. Hydrogen chloride is liberated, and the reaction is considered finished when the evolution of gas ceases. Mono- and disulfonic acids of benzene and naphthalene can be obtained by this procedure, but the product contains varying amounts of the sulfonylchloride because of the unavoidable secondary reaction previously indicated.

Corbellini found that when 1 mole of naphthalene is treated at 15 to 45°C. with 2 moles of chlorosulfonic acid, 1, 5-naphthalenedisulfonic acid is formed, together with varying proportions of the corresponding disulfonylchloride.[1] When CCl_4 is used as a solvent, and naphthalene is treated with either 2 or 4 moles of chlorosulfonic acid, sulfonylchlorides are always formed in addition to the mono- and disulfonic acids. In all cases, naphthalene is attacked only in the 1 and 5 positions. The final yields of the various products depend on the velocities of the different concurrent reactions, which, in turn, are governed by the conditions employed. The reaction leading to the formation of chlorosulfonic acids is favored by low temperatures.

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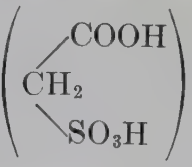
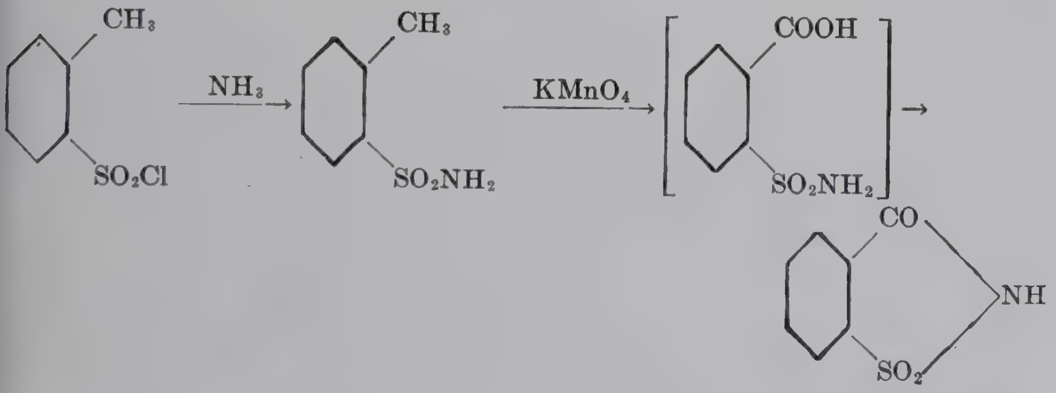
[1] Ger. 530,135 (1930); U. S. 1,871,466 (1932).

[2] Gebler, *J. Chem. Ind.* (*Moscow*), **2,** 984 (1926).

In the aliphatic series, the use of chlorosulfonic acid is illustrated by the following sulfonations: Sulfoacetic acid  $\left(CH_2\begin{matrix}COOH\\SO_3H\end{matrix}\right)$ is obtained by heating acetic and chlorosulfonic acids together. A sulfopropionic acid $CH_3{\cdot}CH(SO_3H)COOH$ is formed by the similar action of chlorosulfonic acid on propionic acid.

Chlorosulfonic acid is employed to advantage in the preparation of *o*-toluenesulfonyl chloride, an intermediate in the preparation of benzosulfimide, *i.e.*, saccharin. The use of chlorosulfonic, although more expensive than sulfuric acid, gives a higher yield (40 per cent of the ortho isomer) and at the same time eliminates the costly conversion of the sulfonic acid to sulfonyl chloride by phosphorus pentachloride that would otherwise be necessary. The para isomer, which is a solid, is readily separated from the desired ortho compound, which is then submitted to further purification.



Chlorosulfonic acid forms sulfamic acids with amines of both the aliphatic and aromatic series. The reaction is carried out in a solvent; *e.g.*, chloroform and acids of the following types are formed:

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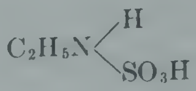
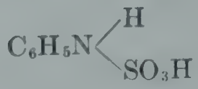
[1] Corbellini, *Giorn. chim. ind. applicata*, **9**, 118 (1927).



$$C_2H_5N\begin{matrix}\diagup H\\ \diagdown SO_3H\end{matrix} \qquad (I)$$



$$C_6H_5N\begin{matrix}\diagup H\\ \diagdown SO_3H\end{matrix} \qquad (II)$$

This reaction is used in the preparation of *o*-anilinesulfonic acid, which is derived through rearrangement of the sulfamic acid (II) by heating in the presence of sulfuric acid. *o*-Sulfonic acids of naphthylamines can be prepared in a similar manner.

Chlorosulfonic acid in an inert solvent can be used advantageously as a means of effecting the ortho sulfonation of aromatic amines.[1] This technic has been employed in the preparation of 1-aminoanthraquinone-2-sulfonic acid, a solvent such as tetrachloroethylene being used. The organic solvent may, however, be replaced by concentrated sulfuric acid (100 per cent) in this particular sulfonation.[2]

In the sulfonation of naphthols, chlorosulfonic reacts similarly to sulfuric at ordinary temperatures. Thus alpha naphthol is converted to the 2-sulfonic acid, and beta naphthol to the 1-sulfonic acid isomer.[3] At higher temperatures, 100°C., the 4-isomer is formed in the case of α-naphthol, and the 6-isomer in the case of β-naphthol-when tetrachloroethane is used as a solvent at 130°.

Fluosulfonic acid, derived by the reaction of hydrogen fluoride and sulfuric acid or preferably by the action of potassium sulfate on hydrogen fluoride,[4] behaves similarly to chlorosulfonic acid. The reagent can be used for the sulfonation of benzene at 100° under pressure, and yields either the sulfonic acid or sulfones. The formation of sulfones increases with elevation of operating temperature and ratio of HF to H_2SO_4

$$HF + H_2SO_4 + RH \rightarrow RSO_3H + RSO_2R + HF + H_2O$$

Fluosulfonic acid may also be used for the conversion of aniline sulfate to sulfanilic acid.[5] It reacts with chloroform but not with carbon tetrachloride.[6]

SULFONATION WITH SULFUR DIOXIDE

The action of SO_2 on aqueous solutions of quinones results in reduction as well as sulfonation.

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[1] U. S. 2,135,346 (1938).

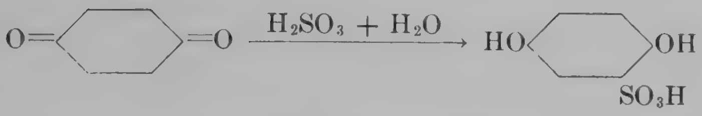
[2] Ogilvie, U. S. 2,360,010 (1944).

[3] VORONTZOV and SOKOLOVA, *Org. Chem. Ind.* (U.S.S.R.), **2,** 399 (1936); VORONTZOV and IVANOVA, *J. Applied Chem.* (U.S.S.R.), **13,** 1470 (1940).

[4] *Z. anorg. allgem. Chem.*, **243,** 39 (1940).

[5] *Die Chemie*, **56,** 333 (1943).

[6] SIMONS, PASSINO, and ARCHER, *J. Am. Chem. Soc.*, **63,** 608 (1941).

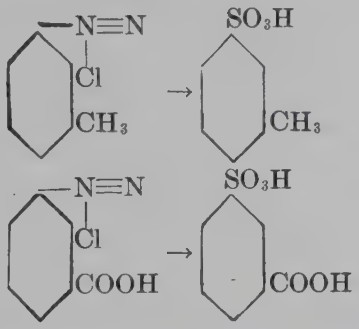


In the treatment of chloroquinones, there is a tendency to form disulfonic acids because of the replacement of a chlorine atom by a sulfonic acid group.[1]

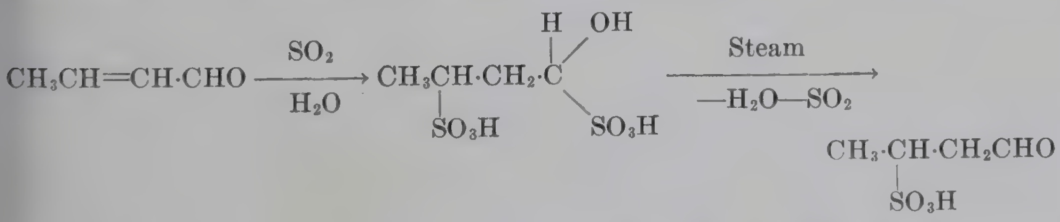
$$C_6H_2Cl_2O_2 + 2H_2SO_3 \rightarrow C_6HCl(OH)_2(SO_3H)_2 + HCl$$

A similar reducing and sulfonating action is observed when 1-nitroso-2-naphthol reacts with sulfurous acid in a boiling alcoholic solution, 1-amino-2-naphthol-4-sulfonic acid being formed.

When diazotized amines in alcoholic solution are treated with sulfur dioxide, sulfonic acids are obtained through the replacement of the diazo group. *m*-Toluenesulfonic as well as *m*-sulfobenzoic acid may be obtained from the corresponding diazotized amines by this procedure.

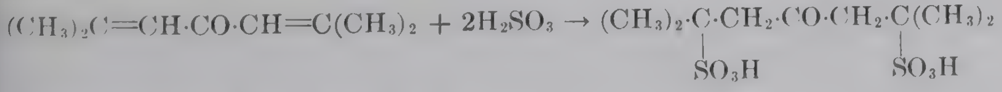


Crotonaldehyde, when treated with aqueous SO_2 at 0°C. and the resulting product boiled in water, gives beta sulfobutyraldehyde:



$$CH_3CH{=}CH{\cdot}CHO \xrightarrow[H_2O]{SO_2} CH_3\underset{SO_3H}{CH}{\cdot}CH_2{\cdot}\underset{SO_3H}{\overset{H\ \ OH}{C}} \xrightarrow[-H_2O-SO_2]{\text{Steam}} CH_3{\cdot}\underset{SO_3H}{CH}{\cdot}CH_2CHO$$

In a similar manner, phorone gives with 6 per cent aqueous SO_2 diisobutyl ketone β, β'-disulfonic acid:[2]



$$(CH_3)_2C{=}CH{\cdot}CO{\cdot}CH{=}C(CH_3)_2 + 2H_2SO_3 \rightarrow (CH_3)_2{\cdot}\underset{SO_3H}{C}{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}\underset{SO_3H}{C}(CH_3)_2$$

Hydrocarbons can also be sulfonated photochemically by sulfur dioxide and chlorine;[3] sulfonyl chlorides are thus produced and can be hydrolyzed to the corresponding sulfonic acids.

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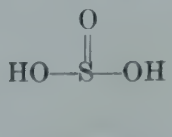
[1] DODGSON, *J. Chem. Soc.*, **1930**, 2498.

[2] *Ber.*, **37**, 4047 (1904).

[3] Fox, Henke, and Reed, U. S. 2,228,598 (1941).

SULFITES AND BISULFITES AS SULFONATING AGENTS

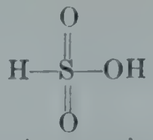
Sulfurous acid has two possible structures:



$$HO-\overset{\overset{\displaystyle O}{\|}}{S}-OH$$

I. Symmetrical

or



$$H-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH$$

II. Asymmetrical

The soluble sulfites possibly exist in both forms but, in their reaction with alkyl halides, sulfonates are formed as follows:

$$KSO_2{\cdot}OK + C_2H_5I \rightarrow C_2H_5SO_2OK + KI$$

The sulfonic acids and their esters may therefore be considered as derivatives of unsymmetrical sulfurous acid. When, however, SO_2 is passed into a solution of an alkali alcoholate, an unstable salt of alkyl sulfurous acid is obtained,

$$SO_2 + C_2H_5OK \rightarrow C_2H_5O{\cdot}SO_2K$$

which easily loses SO_2 and which is isomeric with the stable alkylsulfonate previously mentioned. On heating in the presence of potassium iodide, in alcoholic solution, this unstable salt is converted to the double salt of potassium ethylsulfonate and potassium iodide.

Treatment of Aliphatic Compounds.—It will be recalled that one of the characteristics distinguishing aliphatic from aromatic compounds is their inability to react with sulfuric acid. The formation of aliphatic sulfonic acids is frequently accomplished by heating the alkyl halides with alkali sulfites, methane- and ethanesulfonic acids being prepared in this manner.

This reaction

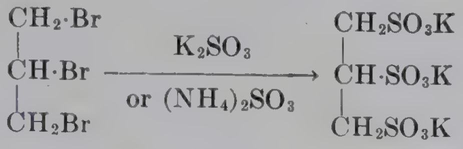
$$RX + (NH_4)_2SO_3 \rightarrow RSO_3NH_4 + NH_4X$$

is known as the *Strecker* reaction and has been used for the preparation of numerous sulfonates by reaction with methyl and ethyl iodides, ethylene bromide, chloroform, chlorinated quinones, benzyl chloride, etc. The procedure is also useful for the preparation of octyl, decyl, myristyl, cetyl, and octadecyl sulfonates from the corresponding bromides, and sodium lauryl sulfonate has been prepared from lauryl chloride.

The essential procedure consists in heating the alkyl halide with an excess of aqueous sodium sulfite solution in an autoclave at about 200° for several hours.[1] The reaction proceeds smoothly, and the yields are almost quantitative for primary halides. It works for some unbranched secondary halides or those in which the branch is remote from halogen but is of little value with highly branched secondary halides. The reaction does not function on tertiary halogens which give olefins.

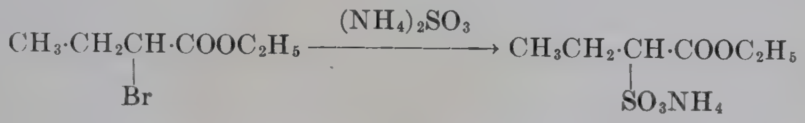
[1] REED and TARTAR, *J. Am. Chem. Soc.*, **58**, 322 (1936).

In its simplest form, the action of sulfites and acid sulfites may be illustrated by the replacement of halogen as in the case of tribromo propane to give propane trisulfonate:



$$\begin{array}{l} CH_2{\cdot}Br \\ | \\ CH{\cdot}Br \\ | \\ CH_2Br \end{array} \xrightarrow[\text{or } (NH_4)_2SO_3]{K_2SO_3} \begin{array}{l} CH_2SO_3K \\ | \\ CH{\cdot}SO_3K \\ | \\ CH_2SO_3K \end{array}$$

The halogen in aliphatic esters also may be replaced. Thus, Backer converted alpha bromobutyric acid ethyl ester to alpha sulfoethyl butyrate.[1]

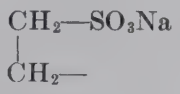


$$CH_3{\cdot}CH_2\underset{\substack{|\\ Br}}{CH}{\cdot}COOC_2H_5 \xrightarrow{(NH_4)_2SO_3} CH_3CH_2{\cdot}\underset{\substack{|\\ SO_3NH_4}}{CH}{\cdot}COOC_2H_5$$

This type of reaction has attained technical significance in the preparation of detergents that are formed by the action of sulfites on the esters derived from the action of chloracetyl chloride on the higher aliphatic alcohols. Thus, cetyl chloroacetate is converted to soluble alkali metal sulfonate by action of alkali metal sulfite.[2] Similarly, β, β′-dichloroethyl ether may be converted to β-chloro-β′-sulfoethyl ether.

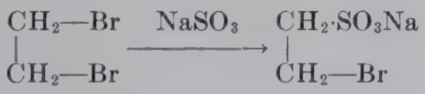
$$ClCH_2CH_2{\cdot}O{\cdot}CH_2CH_2Cl \xrightarrow{Na_2SO_3} Cl{\cdot}CH_2CH_2{\cdot}O{\cdot}CH_2CH_2SO_3Na$$

The resulting product may then be reacted with the alkali metal salt of a long-chain aliphatic carboxylic acid to give products of detergent properties of the general structure $R{\cdot}COO{\cdot}CH_2CH_2{\cdot}O{\cdot}CH_2CH_2SO_3Na$. The radical



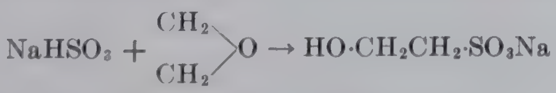
$$\begin{array}{l} CH_2\text{—}SO_3Na \\ | \\ CH_2\text{—} \end{array}$$

may likewise be exploited for preparation of detergents; and for this purpose, ethylene dichloride (or dibromide) is treated with aqueous sodium sulfite:[3]



$$\begin{array}{l} CH_2\text{—}Br \\ | \\ CH_2\text{—}Br \end{array} \xrightarrow{NaSO_3} \begin{array}{l} CH_2{\cdot}SO_3Na \\ | \\ CH_2\text{—}Br \end{array}$$

A reaction that has attained considerable technical importance for the preparation of isethionic acid, an intermediate in the manufacture of wetting agents, involves the action of ethylene oxide on sodium bisulfite.[4]



$$NaHSO_3 + \begin{array}{l} CH_2 \\ CH_2 \end{array}\!\!>O \rightarrow HO{\cdot}CH_2CH_2{\cdot}SO_3Na$$

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[1] Backer, *Rec. trav. Pays Bas.*, **43**, 304 (1924).

[2] Brit. 382,718; Fr. 735, 211; Fr. 735,647.

[3] "Organic Syntheses," Vol. 10, p. 96.

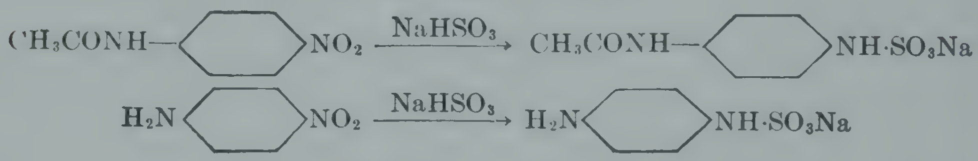
[4] Lauer and Hill, *J. Am. Chem. Soc.*, **58**, 1873 (1936).

When this reaction is conducted so that no appreciable excess of ethylene oxide is ever present, in order to preclude the formation of glycols and resins, the yield and purity of the resulting product are quite high. This method is preferred to that which involves the sulfonation of ethyl alcohol in spite of the care that must be taken to avoid explosion with ethylene oxide when work is being done in an atmosphere of nitrogen.

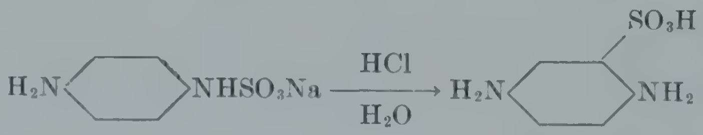
Bisulfite sulfonation of lignin occurs in the manufacture of sulfite wood pulp in the paper industry. Here, the essential feature of the process is the removal of the lignin from the wood as a result of the formation of water-soluble lignin sulfonic acids. So-called alpha and beta lignin sulfonic acids are formed and occur in the liquor as their calcium salts. The alpha lignin sulfonic acid can be precipitated by beta naphthylamine.

Treatment of Aromatic Compounds.—The use of sulfites as a sulfonating agent in aromatic chemistry sometimes offers certain advantages when the compound to be treated contains the nitro group, a halogen atom, or a hydroxyl group or when it is a quinone. When 1-nitronaphthalene reacts with a boiling aqueous-alcoholic solution of ammonium sulfite, 1-aminonaphthalene-4-sulfonic acid is obtained along with some α-naphthylsulfamic acid. To prepare 1-aminonaphthalene-2, 4-disulfonic acid, the nitronaphthalene is heated with a sodium bisulfite solution at 100°C.[1]

The nitroanilides and nitroaniline are converted to sulfamic acid derivatives when acted on by sodium bisulfite:[2]



Upon hydrolysis of these sulfamic acids, the sulfonic group migrates to the ring as follows:



An industrially important application of sulfites related to the replacement of the chlorine atom of 4′-chloro-2-benzoylbenzoic acid by the sulfonic acid group. The reaction is carried out by treating the keto acid with an excess of aqueous 20 per cent sodium sulfite at 170°C. for

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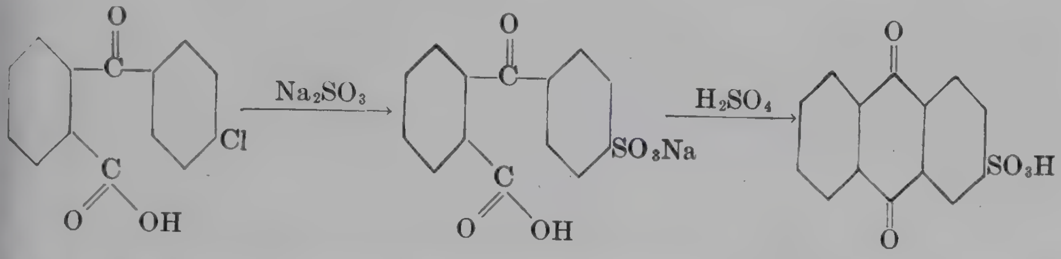
[1] Ger. 92,081 (1895).

[2] WEIL and WASSERMANN, *Ber.*, **55**, 2533 (1922).

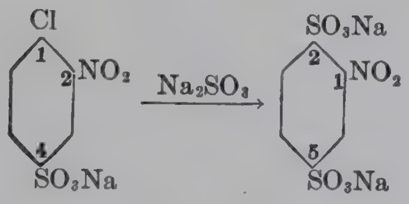
16 hr.[1] The resultant sodium 4′-sulfo-2-benzoylbenzoate is readily cyclized to anthraquinone-2-sulfonic acid.



It will be recalled that direct sulfonation of anthraquinone results in the formation of disulfonic acids and hydroxy impurities when all the anthraquinone undergoes reaction. The 2-aminoanthraquinone obtained by the ammonolysis of the corresponding sodium sulfonate runs uniformly over 99 per cent purity.

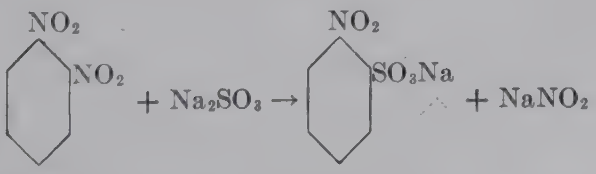
The halogen atom in *p*-bromotoluene is replaced by the sulfonic acid group at 180 to 200°C. by reaction with a 15 per cent solution of sodium sulfite containing a trace of copper sulfate. The chlorine in the side chain can also be replaced, as is evidenced by the formation of toluene-ω-sulfonic acid from benzyl chloride and a concentrated boiling solution of sodium sulfite.

When a nitro or carbonyl group is ortho or para to a halogen atom in the aromatic nucleus, the replacement of the halogen atom takes place much more readily than in the previous examples wherein high temperatures and pressures are required. This reaction may be represented as follows:



Sometimes, the nitro compounds are reduced to amines concurrently with the replacement of the halogen atom by the sulfonic acid group.

This reaction is not restricted to the replacement of a halogen atom; ortho dinitrobenzene behaves similarly.[2]



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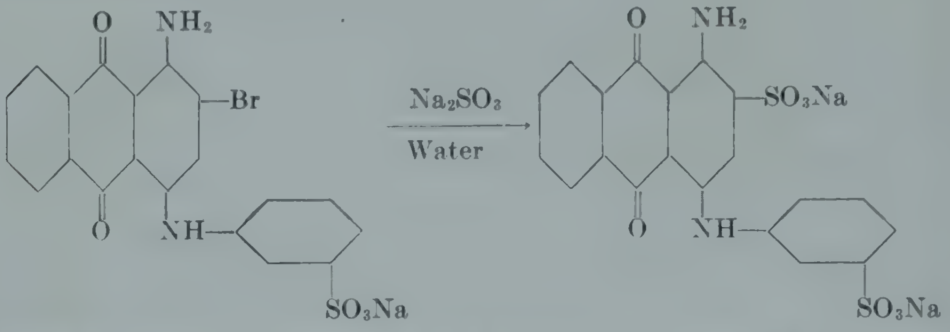
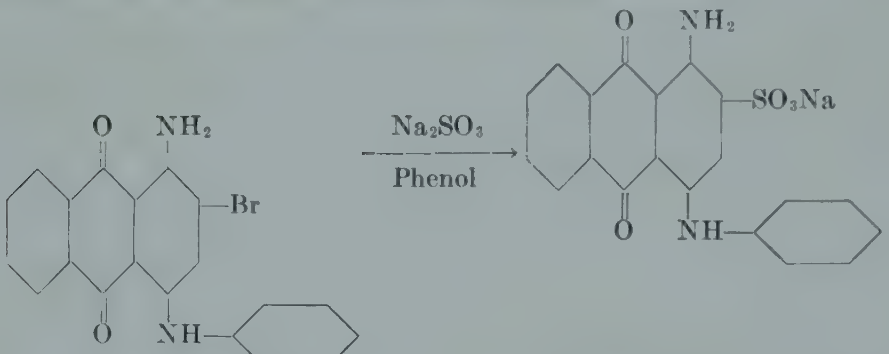
[1] U. S. 1,779,221 (1930).

[2] Fierz-David, "Grundlegenden Operationen der Farbenchemie," 5th ed., p. 107. 1943.

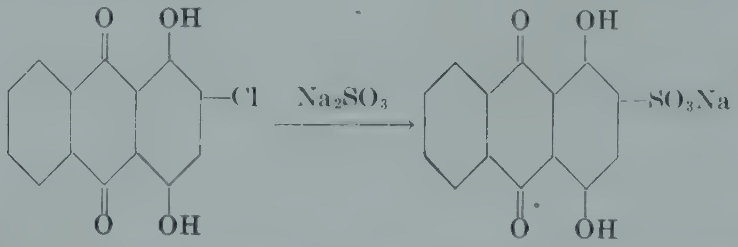
The use of sulfites as a sulfonating agent has attained commercial importance in the field of anthraquinone dyestuffs, as typified by the following examples:


O
NH₂
Br
O
NH
SO₃Na
Na₂SO₃
Water
O
NH₂
SO₃Na
O
NH
SO₃Na

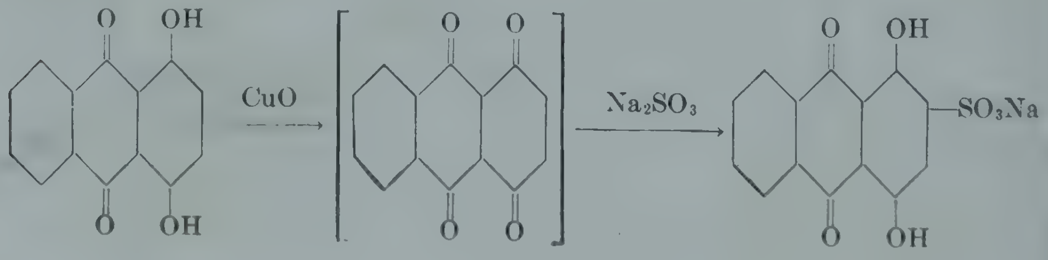
Where the parent material is not soluble in water, a solvent, *e.g.*, phenol, is used as adjunct as in the following illustration.


O
NH₂
Br
O
NH
Na₂SO₃
Phenol
O
NH₂
SO₃Na
O
NH

The action of aqueous sodium sulfite on 2-chloroquinizarine gives quinizarine-2-sodium sulfonate;


O
OH
Cl
O
OH
Na₂SO₃
O
OH
SO₃Na
O
OH

It is, however, not necessary to start with 2-chloroquinizarine since quinizarine gives the same product, but it has been found that copper oxide greatly facilitates the latter reaction, possibly owing to the catalytic formation of quinizarine quinone;


O
OH
O
OH
CuO
O
O
O
O
Na₂SO₃
O
OH
SO₃Na
O
OH

HYPOSULFITES (HYDROSULFITES) AS SULFONATING AGENTS

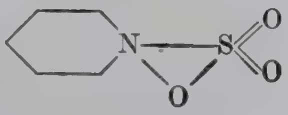
Sodium hyposulfite ($Na_2S_2O_4$)—frequently called sodium hydrosulfite—may be used for the formation of ω-sulfonic and sulfamic acids from either nitro or chloro substituted aromatic compounds. When nitrobenzene is treated with aqueous sodium hyposulfite in the presence of sodium phosphate at 65°C., benzenesulfamic acid is formed according to the following reaction:

$$C_6H_5NO_2 + Na_2S_2O_4 + H_2O \rightarrow C_6H_5NH{\cdot}SO_3Na + NaHSO_4$$

For the production of toluene-ω-sulfonic acid, benzyl chloride is treated with an alkaline solution of sodium hyposulfite in the presence of zinc dust. Dibenzylsulfone is also formed during the reaction.

N-PYRIDINIUMSULFONIC ACID AS A SULFONATING AGENT

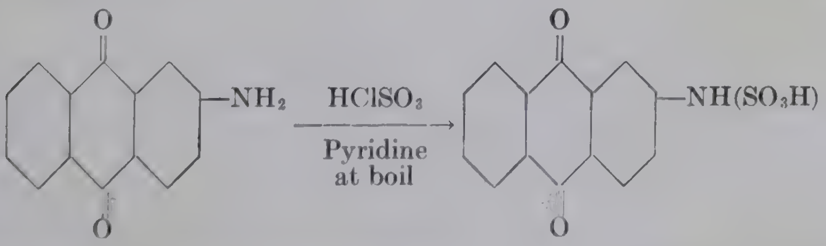
Pyridine reacts with sulfur trioxide and chlorosulfonic acid to form N-pyridiniumsulfonic acid, having the following structural formula:



From a practical viewpoint, it is more convenient to use chlorosulfonic acid rather than sulfur trioxide. It is important that only slightly over 1 mole of $HClSO_3$ in pyridine be employed per mole of amino compound used. This reagent is of general utility and may be employed in the preparation of N-aminosulfonic acids, both aliphatic and aromatic, and for the sulfonation of phenol and naphthalene. Methylamine and acetamide are examples of aliphatic compounds sulfonated by this reagent. When *p*-aminophenol is heated with this sulfonating agent, the sulfamic acid is obtained as the alkali salt upon hydrolysis of the reaction mass. The reaction may be represented as follows:

$$C_6H_4(OH)NH_2 \xrightarrow{C_6H_5N{\cdot}SO_3} C_6H_4(OH)NHSO_3Na$$

This reagent may also be employed in the formation of anthraquinone-2-sodium sulfamate:[1]



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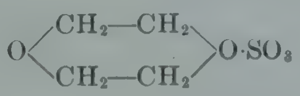
[1] LESNIANSKI, TURSKA—JAROSZEWICZOWA, and ROCZNIKI, *Chem.*, **18**, 680 (1938).

The method of isolation involves drowning the reaction mass in excess of aqueous sodium carbonate and steam-distilling the pyridine. It is important that the mass be kept alkaline during distillation, since the sulfamic acids are readily hydrolyzed.

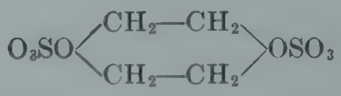
The formation of sulfamic acids has been employed to solubilize difficultly soluble aromatic amino bodies in order to facilitate reactions that must be conducted in an aqueous medium, *e.g.*, diazotization or to promote the dyeing of celanese as, for example, with aminoanthraquinones. Hydrolysis to the parent amine occurs during the dyeing operation.

Dioxane Sulfotrioxide as a Sulfonating Agent

Dioxane forms addition products with sulfur trioxide corresponding to the following compositions:

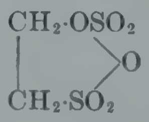


and



Either one of these addition products reacts as a sulfonating agent with no difference in reactivity. The sulfonation reaction is similar to that of pyridiniumsulfonic acid, except that the dioxane sulfotrioxide compounds are much more reactive. In the case of aniline, phenol, and benzoic acid, reaction occurs with substituents rather than the benzene nucleus. Primary alcohols are converted into alkyl hydrogen sulfates, the higher members having valuable detergent properties. Olefins of the straight-chain type are converted into compounds of the carbyl sulfate type.

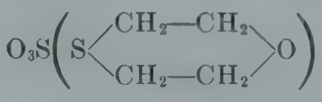
Carbyl Sulfate



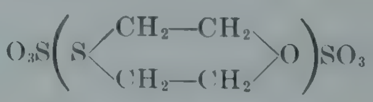
These compounds are then usually hydrolyzed to sulfuric acid and the corresponding beta-hydroxysulfonic acid. However, olefins having a branch chain at the number 2 carbon atom give this carbyl sulfate reaction only in a limited degree, the main products being unsaturated sulfonic acids.[1] Styrene also reacts in this manner.

Unsaturated aliphatic tertiary olefin monosulfonates in which the sulfonate group is attached to a carbon atom having a double bond can also be formed by this method.[2]

Thioxane-sulfur trioxide addition compounds



and



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[1] Bordwell, Suter, and Webber, *J. Am. Chem. Soc.*, **67**, 827 (1945).

[2] U. S. 2,365,783 (1944).

have been found to be useful sulfonating agents, particularly for the sulfonation of olefins.[1] When the addition compound is prepared from thioxane and chlorosulfonic acid, the by-product hydrogen chloride escapes from the reaction mixture, whereas it does not in the case of dioxane. Unlike dioxane, thioxane is only slightly soluble in water, a fact that simplifies its recovery after sulfonation.

USE OF AMINOSULFONIC ACIDS

Aminosulfonic acid ($NH_2{\cdot}SO_3H$) has been used as a sulfonating agent in the treatment of aromatic hydroxy and unsaturated compounds. Styrene may thus be converted when the reaction takes place at 150°C. for 1 hr.

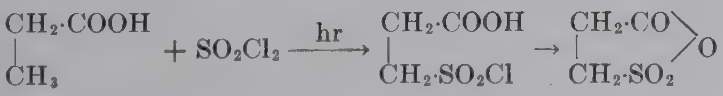
$$C_6H_5CH{=}CH_2 \xrightarrow{NH_2{\cdot}SO_3H} C_6H_5CH{=}CHSO_3H$$

Sulfanilic acid ($NH_2{\cdot}C_6H_4{\cdot}SO_3H$) has also been employed for the conversion of α-naphthylamine to 1-naphthylamine-2-sulfonic acid.

SULFURYL CHLORIDE AS A SULFONATING AGENT

Sulfonation of aliphatic hydrocarbons may be carried out in the presence of light with sulfuryl chloride, SO_2Cl_2, provided that a weak base such as pyridine, quinoline, or thiophenol is used to suppress the chlorination reaction.[2] A 55 per cent yield of cyclohexansulfonyl chloride is obtained treating cyclohexane with this sulfonating agent.

Other hydrocarbons that can be sulfonated by this agent are *n*-butane, ethylbenzene, and *tert*-butylbenzene. The reaction has been extended to include other types of aliphatic compounds, such as propionic, butyric, and isobutyric acids, as well as the higher aliphatic acids, lauric and palmitic acids. The products are the inner anhydrides of the sulfocarboxylic acids[3]



$$\begin{array}{l} CH_2{\cdot}COOH \\ | \\ CH_3 \end{array} + SO_2Cl_2 \xrightarrow{hr} \begin{array}{l} CH_2{\cdot}COOH \\ | \\ CH_2{\cdot}SO_2Cl \end{array} \rightarrow \begin{array}{l} CH_2{\cdot}CO \\ | \\ CH_2{\cdot}SO_2 \end{array}\!\!\!>O$$

Reed has shown that a mixture of chlorine and sulfur dioxide can be used instead of sulfuryl chloride.[4] If the ratio of the two components is adjusted, the reaction can be made to go predominantly via chlorination, chlorosulfonation, or sulfonation.[5]

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[1] Nawiasky and Sprenger, U. S. 2,335,193 (1943); U. S. 2,219,748 (1940).

[2] KHARASCH and READ, *J. Am. Chem. Soc.*, **61**, 3089 (1939).

[3] KHARASCH and BROWN, *J. Am. Chem. Soc.*, **62**, 925 (1940); KHARASCH, CHAO, and BROWN, *J. Am. Chem. Soc.*, **62**, 2393 (1940).

[4] Reed, U. S. 2,046,090; ROSS and POTTER U. S. 2,304,767 (1942); HENKE 2,366,027 (1944); GRUBB and TUCKER 2,374,193 (1945).

[5] See Chap. IV, Halogenation.

DIMETHYL AND DIETHYL SULFATES AS SULFONATING AGENTS

Under certain conditions, these reagents react as both esterifying and sulfonating agents. Thus, diphenylamine is converted to methyl diphenylsulfonic acid with dimethyl sulfate.

METHOXY SULFONCHLORIDE AS A SULFONATING AGENT

This reagent, CH_3OSO_2Cl, reacts with benzene and toluene to give methylsulfonic acids of the type $R{\cdot}SO_3CH_3$ with some RSO_3H and R_2SO_2. It is used particularly for the sulfonation of camphor to produce CH_3-3-camphor-sulfonate.

III. SEPARATION OF SULFONIC ACIDS

An important problem in sulfonation operations is the isolation or separation of the desired products. When only one sulfonic acid derivative is produced, it can generally be isolated as the alkali or alkaline earth salt with good yields and in a high state of purity. When isomers are present, the process of separating the components is often tedious and difficult. In a few cases, the sulfonic acid, because of its low solubility in the residual sulfuric acid, separates out in the reaction mixture. The sulfonic acid derivative of salicylic acid can thus be isolated.[1]

A number of general methods are available for recovering the sulfonic acids from the reaction mixture, and these procedures are susceptible to numerous modifications. Some of the more common methods are the following:

Method I. Dilution of Sulfonation Mixture.—Some isomeric sulfonic acids can be separated by pouring the reaction mass into water and cooling; *p*-toluenesulfonic acid can thus be separated from the ortho isomer.[2] The process is often facilitated by the addition of concentrated hydrochloric acid.

Method II. Neutralization of Reaction Mass.—*a.* When only one sulfonic acid is produced, as in the preparation of benzenesulfonic acid, the charge may be completely neutralized with either marble dust or hydrated lime. In each case, the solution of the sulfonate is removed by filtration. The calcium benzenesulfonate may be converted to the sodium salt by treatment with soda ash.

b. A mixture of sodium and calcium salts may be employed, the former being added in slight excess of the quantity necessary to form the soluble sodium sulfonate, the latter ensuring the conversion of the sulfuric acid to the insoluble calcium sulfate.

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[1] MELDRUM and SHAH, *J. Chem. Soc.*, **123**, 1986 (1923).

[2] DORSSEN, *Rec. trav. chim.*, **29**, 371 (1910).

c. When isomers are present, advantage may sometimes be taken of the difference in solubility of the calcium salts. Thus, after the removal of the gypsum, the calcium salt of naphthalene-2-sulfonic acid, which is less soluble than the alpha isomer, separates out from the filtrate.

d. Sometimes, an alkaline earth salt of a sulfonic acid can be separated from a mixture of the sodium salts. By adding the correct quantity of barium chloride to a solution containing sodium phenanthrenesulfonates, the barium salt of phenanthrene-2-sulfonic acid is precipitated.[1]

Method III. Fractional Precipitation.—*a.* The precipitation of sodium sulfonates from the reaction mass by the addition of sodium chloride is due, in most cases, to their slight solubility in the excess of sulfuric acid. In many instances, the addition of equivalent quantities of sodium sulfate, nitrate, or acetate serves equally well for the precipitation of the sodium salt. When soluble metallic salts of Cu, Zn, Ni, etc., are employed, almost theoretical yields of the insoluble metal sulfonate can be obtained.

b. In the production of 1, 5-naphthalenedisulfonic acid, the isomeric 1, 6-disulfonic acid is also formed. By the addition of sodium chloride to the mixture of acids, the difficultly soluble acid sodium salt of 1, 5-naphthalene disulfonic acid separates out. The acid sodium salts of benzoic-3-sulfonic and salicylic-5-sulfonic acids can similarly be precipitated because of their meager solubility in the residual sulfuric acid.

c. Sodium chloride may be added to a solution containing isomeric sodium sulfonates, and the introduction of the common ion so diminishes the solubility that one of the isomers is thrown out. β-naphthalenesulfonic acid can thus be separated from the alpha isomer.

Method IV. Formation of Basic Salts.—In some cases, it is advisable to use a relatively insoluble basic salt for the separation of a sulfonic acid. This method is applicable to sulfonic acids containing hydroxyl groups. A mixture of R and G acids, *i.e.*, 2-naphthol-3, 6 and 6, 8-disulfonic acids, respectively, is treated with lime to permit the separation of the calcium disulfonates from the gypsum. The filtrate of calcium naphtholdisulfonates is treated with a base, *e.g.*, NH_4OH, to convert the neutral into basic salts, and the less soluble basic calcium salt of R acid crystallizes out. The mother liquor is then treated with ammonium sulfate. The calcium sulfate is removed by filtration, and the ammonium salt of 2-naphthol-6, 8-disulfonic acid is obtained after concentration of the filtrate to effect crystallization.

Method V. Formation of Sulfonchlorides.—In some cases where fractional preciptations fail, it is feasible to form the sulfonchlorides and then separate these by fractional crystallization. The sulfonchlorides may then be reconverted to the corresponding acids by boiling with water. Toluene-2, 5-disulfonic acid can be separated from the 3, 5-isomer in this manner. The barium disulfonates are treated with phosphorus pentachloride, and the sulfonchlorides are separated by recrystallization from carbon disulfide.

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[1] Fieser, *J. Am. Chem. Soc.*, **51**, 2460 (1929).

It must be understood that none of the above methods is general in its application. Many specific procedures have been devised for individual operations; the Dennis process for extracting benzenesulfonic acid with benzene (page 315) constitutes an interesting example of such special methods of separation.

IV. PHYSICAL AND CHEMICAL FACTORS IN SULFONATION

The preceding survey has indicated that the products resulting from sulfonation depend upon a number of factors and that these may affect not only the degree but also the course of the reaction. Some of the more important of these factors for a particular sulfonation are

Concentration of the sulfonating agent.
Temperature of the reaction.
Time of reaction.
Catalysts and sulfonation aids.
Agitation.

Relation of SO_3 Concentration to Sulfonation.—When sulfuric acid is employed, it is known that the sulfonation reaction stops at a definite SO_3 concentration, different for each compound undergoing treatment. Guyot designated the limiting SO_3 concentration by the Greek letter π; and he found that in the preparation of benzenesulfonic acid, sulfonation stopped regardless of temperature, agitation, or catalysts when the value of π is 64 per cent corresponding to the hydrate $H_2SO_4 \cdot 1.5H_2O$.[1] In practice, no action takes place after the acidity reaches 66.4 per cent SO_3. Considerable acid is thus obviously wasted by ordinary methods of sulfonation. When 100 per cent sulfuric acid is used, only 55 per cent of the available sulfur trioxide is utilized in the reaction, this value being reduced to 40 per cent with the employment of 94 per cent H_2SO_4.

This situation has led to the use of stronger acids, which, however, result in the formation of disulfonic acids. Novel procedures have therefore been devised and employed to eliminate the water of reaction as it is formed, and some of these methods are discussed later on pages 312 *et seq.*

In the sulfonation of naphthalene, Regnault found that sulfonation ceases at a definite residual acidity.[2] The values for π for naphthalene mono-, di-, and trisulfonation, as determined by Courtot, are as follows:[3]

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[1] GUYOT, *Chimie & industrie*, **2**, 879 (1919).

[2] REGNAULT, *Ann. chim. phys.*, [2] **65**, 87 (1837).

[3] COURTOT, *Compt. rend.*, **182**, 855 (1926).

For naphthalene monosulfonation at 55 to 60°C. = 53% SO_3
For naphthalene monosulfonation at 160° = 52% SO_3
For naphthalene disulfonation at 10° = 82% SO_3
For naphthalene disulfonation at 80 to 90° = 80% SO_3
For naphthalene disulfonation at 160° = 66.5% SO_3
For naphthalene trisulfonation at 160° = 79.8% SO_3

The value of π is here shown to be a function of the reaction temperature. Courtot demonstrated further that naphthalenedisulfonic acids form addition compounds with sulfur trioxide, these being capable of giving up SO_3 slowly to naphthalenemonosulfonic acid which is present. Therefore, for some sulfonations, π depends also on the sulfur trioxide fixed in a labile state, and calculations for complete sulfonation should take into account the formation of the addition compound.

The ease with which different compounds are sulfonated varies considerably. Benzene can be sulfonated with acids stronger than 64 per cent $SO_3 \asymp 78.4$ per cent H_2SO_4; naphthalene, with acids stronger than 52 per cent $SO_3 \asymp 63.7$ per cent H_2SO_4; and anthracene is readily converted to the monosulfonic acid with sulfuric acid containing 43 per cent $SO_3 \asymp 53$ per cent H_2SO_4. For the sulfonation of anthraquinone, however, practical considerations dictate the use of oleum, because the employment of concentrated sulfuric acid at 200 to 250°C. entails difficulties in operation as well as losses in yield due to oxidation. In the preparation of anthraquinonedisulfonic acids from the monosulfonic acid, the reaction does not proceed satisfactorily unless the concentration of free SO_3 is in excess of 3 per cent. The effect of SO_3 concentration on the rate and degree of sulfonation in the treatment of anthraquinone is shown by the appropriate curves of Figs. 10 and 11.[1]

In general, disulfonation and trisulfonation require increasingly greater concentrations of sulfur trioxide. Not only must the acid concentration be greater, but the acid ratio must be larger and the operating temperature higher.

When only the monosulfonic acid is desired, and the equilibrium between the mono- and disulfonic acid is such that large proportions of the latter are obtained, it is customary to resort to partial sulfonation. Thus, in the sulfonation of anthraquinone, 16 per cent of disulfonic acids is obtained when 75 per cent of the acid theoretically necessary for complete monosulfonation is employed, and 21 per cent of disulfonic acids is obtained with the stoichiometric quantity of acid. Practical considerations, therefore, dictate the most suitable ratio of reactants, since the unconverted anthraquinone must be recovered.

Since the value of π is greater for disulfonations than for the formation of the monosulfonic acid, it is often good practice to feed the sulfonating acid gradually throughout the run. This technic provides a medium wherein the SO_3 concentration is sufficiently low to inhibit to a considerable extent the formation of disulfonic acids.

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[1] **Lauer**, *J. prakt. Chem.*, **130**, 185 (1931).

Evidence that the orientation of sulfonic acids is to some extent influenced by the acid concentration has been obtained by Holleman and Polak.[1] When barium *m*-benzenedisulfonate is heated at 209°C. with oleum containing 12.5 per cent SO_3, 2 per cent of the product is converted to the para isomer; similar treatment with 98 per cent sulfuric acid results in the formation of 11.1 per cent of *p*-benzenedisulfonic acid.

Effect of the Reaction Temperature.—An increase in the sulfonation temperature accelerates both the rate and degree of reaction. Since the tendency to polysulfonation is increased with a rise in temperature, practical considerations dictate the use of thermal conditions and proportions of the reactants that produce a minimum of undesirable reaction products. The temperature of sulfonation may also play an important role in the orientation of the sulfonic acid groups. In the preparation of *m*-benzenedisulfonic acid or anthraquinonemono- or disulfonic acids, the orientation of the substituents is practically unaffected by the reaction temperature, but this factor does play an important role in the sulfonation of toluene and naphthalene derivatives.

In the monosulfonation of toluene, all three isomers are formed, but a rise in the reaction temperature favors the formation of the para acid at the expense of the ortho isomer. The data of Holleman and Caland are given in Table IV.[2] The meta acid undergoes practically no change; but in the presence of a large excess of sulfuric acid at 100°C., the ortho acid is transformed in part to the para isomer. A further illustration of the orientating influence of temperature in the toluene series is the sulfonation of 6-chloro-*o*-toluidine. At 140 to 200°C., the formation of the 5-sulfonic acid is favored, whereas a temperature of 100°C. or under is conducive to the formation of the 3-sulfonic acid.

TABLE IV.—EFFECT OF TEMPERATURE ON SULFONATION OF TOLUENE

Isomer	0° %	35° %	75° %	100° %
Ortho	42.7	31.9	20.0	13.3
Meta	3.8	6.1	7.9	8.0
Para	53.5	62.0	72.1	78.7

The orientating influence of the reaction temperature is brought out in a striking manner in the formation of naphthalene-, naphthol-, and naphthylaminesulfonic acids. In the monosulfonation of naphthalene, the proportions of alpha and beta acids formed at different temperatures are the following:[1]

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[1] HOLLEMAN and POLAK, *Rec. trav. chim.*, **29,** 416 (1910).

[2] HOLLEMAN and CALAND, *Ber.*, **44,** 2504 (1911).

Temperature, °C.	Alpha, %	Beta, %
40	96.0	4.0 (Fierz-David)*
80	96.5	3.5
90	90.00	10.0
100	83.0	17.0
110.5	72.6	27.4
124	52.4	47.6
129	44.4	55.6
138.5	28.4	71.6
150.0	18.3	81.7
161.0	18.4	81.6
160.0	15.0	85.0 (Fierz-David)*

Naphthalene and 100 per cent sulfuric acid in equimolecular proportions were heated at the temperatures noted for a period of 8 hr.

* Fierz-David, "Grundlegende Operationen der Farbenchemie," 1924.

The data of Euwes indicate that α-naphthalenesulfonic acid is the primary product, this being transformed to the more stable beta isomer at higher temperatures.

According to Fierz-David and Hasler, the following conclusions may be drawn from experimental data on the disulfonation of naphthalene:[2] Under 40°C., about 70 per cent of naphthalene-1, 5-disulfonic acid and 25 per cent of the 1, 6-isomer are formed in practically constant proportions, together with traces of the 2, 7-acid. As the temperature of sulfonation is raised, the proportion of the 1, 5-acid diminishes, owing to replacement by 1, 6- and 2, 7-acids; and at 135°C., the 1, 5-acid is no longer present in the reaction mixture. At 140°C., the 2, 6-acid begins to appear; and at 165°C., the reaction mixture contains about 25 per cent of the 2, 6-acid, 65 per cent of the 2, 7-acid, and 10 per cent of the 1, 6-acid.

These temperature orientation relationships are brought out in Fig. 3, page 267, which includes also the course of the reactions leading to the formation of naphthalenetrisulfonic acids.

On sulfonating β-naphthol, the reaction temperature again plays an important role. Below 15°C., Crocein acid (2-naphthol-8-sulfonic acid) is the principal product; but at 80°C., this is transformed to Schäffer acid (2-naphthol-6-sulfonic acid). Similarly, when Schäffer acid is further sulfonated, R and G acids, *i.e.*, the 2, 3, 6- and 2, 6, 8-naphtholdisulfonic acids, are obtained, the proportions of R acid being greater when the sulfonation is carried out at 100°C. G acid predominates if the reaction is conducted under 35°C.

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[1] Euwes, *Rec. trav. chim.*, **28**, 298 (1909).

[2] Fierz and Hasler, *Helvetica Chim. Acta*, **6**, 1133 (1923).

β-Naphthylamine on sulfonation with three parts of sulfuric acid monohydrate yields a mixture of monosulfonic acids the composition of which varies with the reaction temperature.[1] At temperatures under 100°C., a mixture comprising 60 per cent of 2-naphthylamine-5-sulfonic acid and 40 per cent of the 2, 8-isomer is obtained, along with traces of the 6- and 7-sulfonic acids. A sulfonation temperature of 150°C. leads to the formation of about equal quantities of 2-naphthylamine-6- and 7-sulfonic acids.

In the anthraquinone series, the temperature of sulfonation is without influence on the position taken by the first sulfonic acid group, but it does exercise a slight orientating influence in the preparation of the 2, 6- and 2, 7-anthraquinonedisulfonic acids. At 120°C., the proportions are 26 per cent of the former and 52 per cent of the latter; but at 180°C., the proportions are approximately 40:45. These relationships are brought out graphically by the temperature curves of Fig. 10, page 281.

Although migrations of the sulfonic acid group with rising temperature are common in the naphthalene series, no such action has been observed with respect to the anthraquinonesulfonic acids. Without the presence of a mercury catalyst, substitution takes place practically exclusively in the beta positions, and an increase in the reaction temperature leads to the formation of disulfonic acids and oxidation compounds.

Relations of Temperature, Hydrolysis, and Sulfonation.—When naphthalene-1, 6-disulfonic acid is heated with sulfuric acid under conditions of temperature and acid concentration that are too low for hydrolysis of the α-sulfonic acid group, no change takes place. If both of these factors are sufficiently great to hydrolyze the sulfonic acid but insufficient for the sulfonation of naphthalene, hydrolysis (desulfonation) occurs but not sulfonation. When the temperature is high enough and the SO_3 concentration sufficient for sulfonation, then new sulfonic acids are formed.[2]

Oxidation and Its Relation to the Sulfonation Temperature.—Because concentrated sulfuric acid and sulfur trioxide exercise an oxidizing action, and since this characteristic is accentuated at higher temperatures, it is advantageous to carry out sulfonations at the lowest practical temperature.

The sulfonation of aromatic amines, as, *e.g.*, the preparation of sulfanilic and naphthionic acid, always gives evidence of oxidation through the presence of free carbon in the diluted reaction mass. In the disulfonation of anthraquinone from 2 to 5 per cent hydroxyanthraquinonesulfonic acids are formed,[3] the lesser quantity being obtained by heating slowly at the start and gradually raising the temperature to 120 to 130°C.

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[1] GREEN and VAKIL, *J. Chem. Soc.*, **113**, 35 (1918).

[2] HODGSON, *Z. Farben-Ind.*, **20**, 124 (1929).

[3] LAUER, *J. prakt. Chem.*, **130**, 213 (1931).

Influence of Reaction Time.—The influence of reaction time is probably best indicated by the curves relating to the sulfonation of anthraquinone (Figs. 9 to 11). In general, it can be stated that prolonging the reaction beyond the conversion period results in the formation of impurities that although small in quantity may be difficult to remove. Where polysulfonation is possible, the disulfonic acids will be formed at the expense of the monosulfonic acids, and, when only the latter are desired, it is necessary to stop the reaction at some point before equilibrium has been reached.

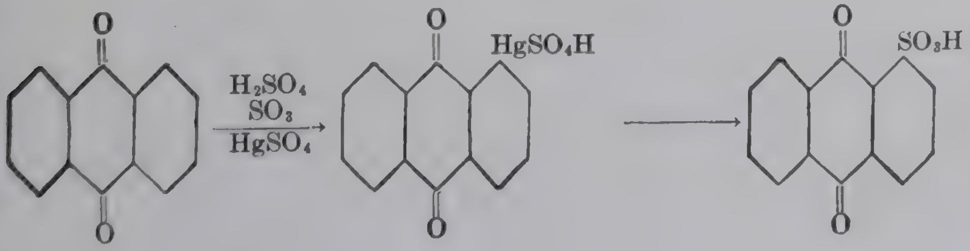
When rearrangements or migrations are possible, a prolonged reaction period will favor the completion of such intramolecular changes. Thus, in the preparation of 2, 7- and 2, 6-naphthalenedisulfonic acids, it is known that the proportion of the 2, 6-acid is increased when the period of sulfonation is prolonged beyond 2 hr. at 165°C.

Effect of Catalysts and Sulfonation Aids.—In the sulfonation process, certain substances such as mercury compounds may catalyze the formation of specific products; *i.e.*, they exercise an orientating effect; or in the case of vanadium compounds, they may merely accelerate the normal reaction without having influence on the positions taken by the sulfonic acid groups. Thus, in some sulfonations, the presence of a catalyst is absolutely essential, whereas in others its value may range from a convenience to an economic advantage.

Some of the substances that have been employed to catalyze sulfonations are the following:

1. Mercury and its salts.
2. Vanadium, its oxides and salts and bisulfates.
3. Alkali carbonates and sulfates.
4. Boric acid and boron trifluoride.

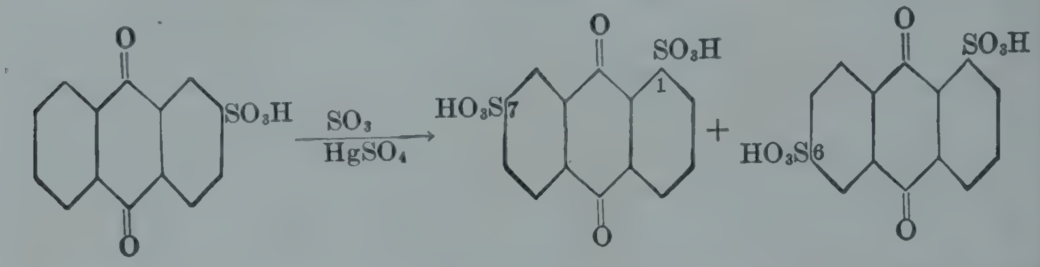
Use of Mercury.—The ordinary sulfonation of anthraquinone results in almost the exclusive formation of beta derivatives. In the presence of mercury or its salts, the alpha derivatives are formed almost wholly. The products of sulfonation by these two procedures are shown on pages 278 and 283. This catalytic activity is attributed to the preliminary formation of a mercury sulfate compound with anthraquinone thus:



Lauer confirmed this view experimentally by showing that the unconverted anthraquinone from catalytic monosulfonation contained organically bound mercury and further demonstrated that this material would, on further treatment with oleum, yield anthraquinone-1-sulfonic acid as the principal product.[1]

When the α-monosulfonic acid is further sulfonated in the presence of mercury, the 1, 5- and 1, 8-disulfonic acids are obtained.

The further sulfonation of anthraquinone-2-sulfonic acid in the presence of mercury results in the formation of α, β-disulfonic acids, thus:



Similarly, the treatment of mercury-free anthraquinone-1-sulfonic acid leads principally to the 1, 6- and 1, 7-disulfonic acids. These observations lead to the conclusion that only one of the alpha positions in the anthraquinone nucleus is affected during each stage of the sulfonation.

The data in Table V show that it is immaterial what mercury compound is employed, all the salts giving substantially the same results

Table V.—Preparation of Anthraquinone-1-sulfonic Acid. Effect of Mercury Salt

Anthraquinone, 208 Gm. Oleum, 25 Per Cent SO_2 (105 Per Cent of Theory); Temperature, 140°C.; Time, 3 Hr. at Operating Temperature

Expt. No.	Catalyst = 1 % Hg	Conversion, %	Fraction I		Fraction II		Residual acids, %
			Grams[1]	%[2]	Grams	%	
1	Hg metal...........	74.8	180.5	55.4	9.8	3.0	16.4
2	Sulfate.............	75.3	178.4	54.8	9.3	2.8	17.7
3	Sulfate.............	74.4	181.8	55.7	8.8	2.7	16.0
4	Chloride″(ic).......	74.6	179.8	55.2	9.2	2.8	16.6
5	Chloride′(ous)......	74.8	181.4	55.6	9.9	3.0	16.2

[1] Grams of K salt.
[2] Based on anthraquinone used.

when the equivalent of 1 per cent by weight of mercury is employed. An increase over this proportion of mercury does not appreciably repress the formation of the beta isomer unless the SO_3 concentration of the sulfonating acid is reduced to 5 per cent (Table II, page 282).

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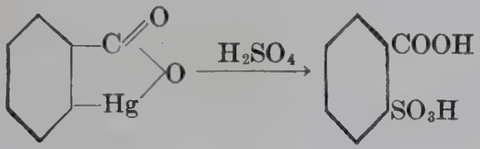
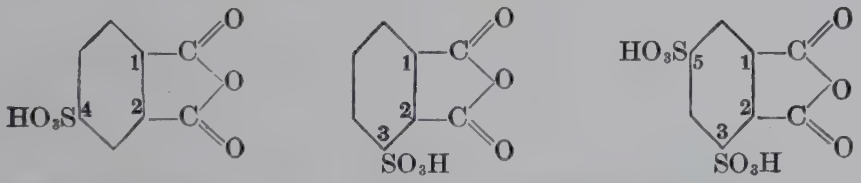
[1] Lauer, *J. prakt. Chem.*, **130**, 231 (1931).

Stimulated by the discovery[1] of the catalytic activity of mercury in the sulfonation of anthraquinone, its use was investigated in many other reactions. Goldberg applied the use of mercuric sulfate to the sulfonation of chloranthraquinones.[2] He found, for example, that whereas 1-chloroanthraquinone yielded 6- or 7-sulfonic acids without a catalyst, with mercuric sulfate the 4- or 4,5- positions were taken by the sulfonic groups. It is known that many organic compounds may be mercurated, and in the aromatic series the mercury generally takes a position *ortho* to a substituent already present. During subsequent treatment with concentrated sulfuric acid, the mercury is replaced by the sulfonic acid group, thus:



When the presence of mercury is practically without effect, it is assumed that sulfonation occurs more readily than mercuration.

α-Naphthol sulfonated in the presence of 20 per cent by weight of mercury sulfate gives 1-naphthol-2-sulfonic acid as the principal product.[3] Ordinary sulfonation of phthalic anhydride with sulfur trioxide yields 4-sulfophthalic anhydride; whereas in the presence of mercury sulfate, the 3-sulfo- and 3, 5-disulfophthalic anhydrides are obtained.



Normal Sulfonation Catalytic Sulfonation

The orientating influence of mercury in the sulfonation of aromatic compounds has been summarized by Lauer as follows:[4]

1. Mercury and its salts, especially the sulfate, which is known to be effective, dissolve only slowly in concentrated sulfuric acid and in oleum.
2. Mercury sulfate combines slowly with the organic components to form an intermediate addition product of sulfonation.
3. In the presence of aqueous sulfuric acid, the organic mercury compound either does not form or is not stable.

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[1] Iljinsky, *Ber.*, **36**, 4194 (1903); Schmidt, *Ber.*, **37**, 66 (1904); Ger. 228,876 (1910).

[2] Goldberg, *J. Chem. Soc.*, . **1931,** 1771

[3] Holdermann, *Ber.*, **39,** 1266 (1906).

[4] Lauer, *J. prakt. Chem.*, **138,** 81 (1933).

4. Normal as well as abnormal products of sulfonation are formed in the presence of mercury, as can be seen from the data below:

Compound sulfonated	Concentration oleum %	Temp., °C.	Hg, %	Yield, %		
				Ortho	Para	Meta
Nitrobenzene	20	90	0	..	3	97
Nitrobenzene	20	90	5	..	25	75
Benzoic acid	10	150	0	..	14	86
Benzoic acid	10	150	5	5	26	69
Benzenesulfonic acid	20	200	0	..	5	95
Benzenesulfonic acid	20	200	5	..	31	69

The remarkable orientating influence of the acid concentration when sulfonating in the presence of mercurous chloride is evident from the following data:

HgCl,[1] addition compound of	Concentration of sulfuric acid	Sulfonic acids obtained, %		
		Ortho	Para	Meta
Nitrobenzene	92	..	5	95
Nitrobenzene	20 % SO_3	94	..	6
Benzoic acid	92	..	8	92
Benzoic acid	10 % SO_3	97	..	3

[1] Obtained by treating organic compound in 100 per cent H_2SO_4 with 5 per cent its weight of mercury as chloride.

Use of Vanadium.—In the disulfonation of benzene with concentrated sulfuric acid, vanadium pentoxide accelerates the rate of reaction but does not alter the position of the substituents.[1] Anderau likewise ascertained that the sulfonation of anthraquinone proceeded somewhat more rapidly in the presence of vanadium sulfate.[2]

Use of Alkali Salts.—In the disulfonation of benzene, it was found that sodium carbonate catalyzed the rate of reaction.[3] Fierz points out, however, that the addition of soda ash to the substance to be sulfonated is made solely for the purpose of preventing lump formation on mixing with sulfuric acid; the mixture is broken up by the carbonic acid liberated, and very small quantities of sodium carbonate suffice.

Lauer has found that the introduction of sodium sulfate in the sulfonation of anthraquinone increases the ratio of monosulfonic acid to disulfonic acid and decreases the percentage conversion of anthraquinone to sulfonic acids.[1] He has also investigated the action of bisulfates on the sulfonation of anthraquinone and found that sulfuric acid sulfonations were accelerated by bisulfates up to certain limits (2 moles bisulfate per mole anthraquinone) and then the reaction decreased in speed. The action is attributed to the formation of pyrosulfates.

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[1] SENSEMAN, *Ind. Eng. Chem.*, **13**, 1124 (1921).

[2] ANDERAU, Diss. E.T.H., Zurich (1923).

[3] SENSEMAN, *loc. cit.*

Sodium sulfate has been found to have an influence on anthraquinone disulfonations by inhibiting alpha sulfonation and hydroxysulfonic acids.[2]

Boric acid has been used as a catalyst in the sulfonation of β-naphthol. Here the presence of boric acid causes no changes in the usual substitution products obtained but does contribute to higher yields of 2-naphthol-1-sulfonic acid and 2-naphthol 1, 6-disulfonic acids at the expense of the 2-naphthol-8- and 2-naphthol-6-sulfonic acids.

Sulfonation Aids.—Acetic and phosphoric anhydrides have been used advantageously as sulfonation aids. When the mono- and dihydric phenols and their ethers are treated with a mixture containing acetic acid, acetic anhydride, and molecular proportions of sulfuric acid, the sulfonic acids are formed almost quantitatively.[3] Acetic anhydride has also been employed in conjunction with oleum in the sulfonation of propylene, trichloroethylene, etc.[4]

Sulfur dioxide finds use as an aid in carrying out a number of sulfonations, carbyl sulfate being thus obtained by the action of SO_3 in sulfur dioxide on ethylene. Such a mixture is also used in the sulfonation of arylalkanes.

Boron trifluoride is a valuable sulfonation aid. It involves the use of gaseous boron fluoride and depends upon the formation of $BF_3 \cdot H_2O$ in the reaction mixture, thereby increasing the SO_3 concentration. After the reaction is over, by the addition of enough water to form $BF_3 \cdot 3H_2O$, the latter can be distilled out under vacuum. Benzene, toluene, naphthalene, phenol, carbazole, and diphenyl have been sulfonated successfully with the aid of boron trifluoride. When beneficial, the use of this sulfonation aid avoids the need of excessive quantities of acid, permits lower reaction temperatures, and increases rate of reaction.

Effect of Agitation.—Experience has demonstrated that efficient agitation is one of the principal requisites of good sulfonation practice. For example, in the sulfonation of benzene, there is a tendency for the benzene and sulfuric acid to separate into layers, and it is obvious that satisfactory results cannot be obtained unless a means is provided to obtain an intimate mixture of the reactants. Even in reactions where solutions or emulsions are more or less readily formed, as for example, naphthalene in concentrated sulfuric acid and nitrobenzene in oleum, it is necessary to provide a practically homogeneous reaction mass, because local differences in temperature or acid concentration may give rise to the formation of undesirable isomers, polysulfonic acids, sulfones, and charred material.

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[1] LAUER, *loc. cit.*

[2] Rogers, U. S. 1,963,383 (1934).

[3] FRIESE, *Ber.*, **64B**, 2103 (1931).

[4] U. S. 2,037,229 (1942).

V. FORMATION OF ADDITION COMPOUNDS IN SULFONATION

The treatment of organic substances with sulfuric acid appears to proceed through the preliminary formation of addition compounds before reaction resulting in the production of sulfonic acids takes place. The experimental evidence[1] of compound formation is largely limited to substances containing oxygen, and here the addition reaction is practically instantaneous, even at temperatures of 0 to 100°C. Some of the addition compounds can be isolated; thus, *p*-cresol with sulfuric acid (molar ratio, 1:2) forms a white crystalline isolable mass which melts at 93.5°C.

Kendall has made a systematic survey of addition compound formation in the systems[2]

$$H_2SO_4 + \left\{\begin{array}{l}\text{organic acids}\\ \text{aromatic aldehydes}\\ \text{aromatic ketones}\\ \text{aromatic phenols}\end{array}\right.$$

Evidence for the existence of compounds in solution was obtained from freezing-point measurements. The principle involved is as follows: When a pure substance A is added to a second pure substance B, the freezing point of the latter is lowered; similarly, the addition of B lowers the freezing point of A. Plotting temperature against concentration gives two curves that intersect at the eutectic point. If, however, a compound AB is formed, this also acts as a pure substance, and its freezing point is lowered by the addition of either A or B.

The freezing-point curves exhibit, therefore, a maximum or a series of maxima that, when referred to the axis of molecular concentration, indicate the composition of the addition compounds formed. From the shape of the curves at the maximum point, it is possible to judge very approximately the amount of compound formed, since a rapid decrease in the temperature of fusion of a compound on addition of either component indicates extensive compound formation in solution.

In Figs. 12 and 13 are shown some of the curves obtained with systems comprising phenols, ketones, carboxylic acids, and H_2SO_4, and it can be seen that some of these possess well-defined maxima.

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[1] Kendall and Carpenter, *J. Am. Chem. Soc.*, **36**, 2498 (1914); Hoogewerff and Van Dorp, *Rec. trav. chim.*, **18**, 211 (1899); **21**, 353 (1902).

[2] Kendall, *J. Am. Chem. Soc.*, **36**, 1722 (1914); Kendall and Booge, *J. Am. Chem. Soc.*, **38**, 1712 (1916).

Addition compounds of the type A_2B, (A being the organic substance; B, the sulfuric acid), AB (or A_2B_2), A_2B_3, and A_2B_4 can be obtained.

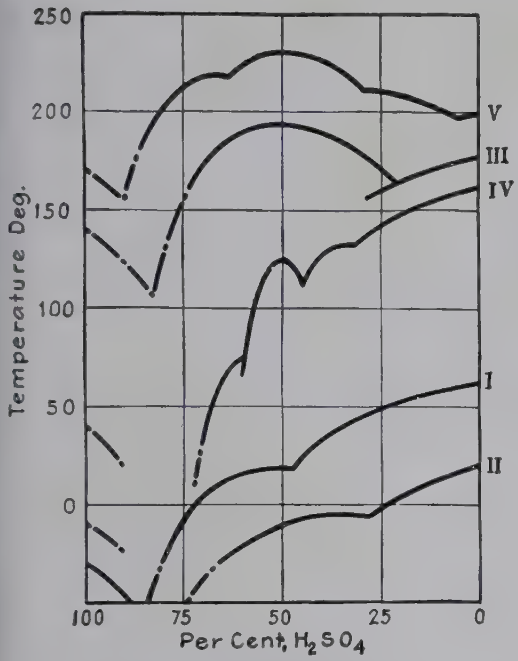


FIG. 12.—Freezing points.

Systems: H_2SO_4 +
- I. *o*-Toluic acid. Add 40° to temperature scale.
- II. Phenol. Add 20° to temperature scale.
- III. Benzophenone. Subtract 130° from temperature scale.
- IV. Dimethylpyrone. Subtract 30° from temperature scale.
- V. Benzoic anhydride. Subtract 160° from temperature scale.

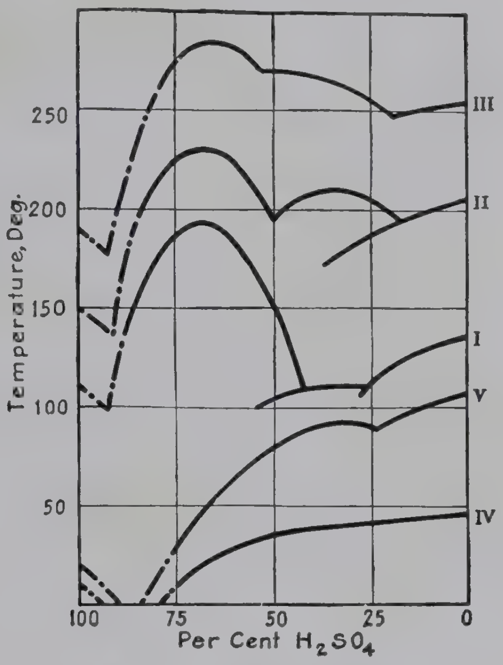
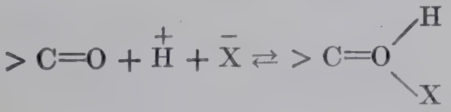


FIG. 13.—Freezing points.

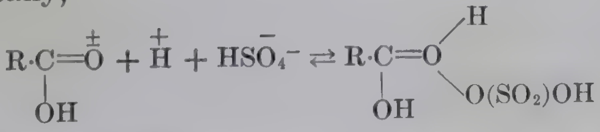
Systems: H_2SO_4 +
- I. *p*-Cresol. Subtract 100° from temperature scale.
- II. *o*-Xylenol. Subtract 140° from temperature scale.
- III. *p*-Xylenol. Subtract 180° from temperature scale.
- IV. *o*-Nitrophenol. Temperature scale correct.
- V. *m*-Nitrophenol. Subtract 10° from temperature scale.

It is apparent that the compounds form a regular series in four steps and are explained on the basis of oxonium salt formation, thus:



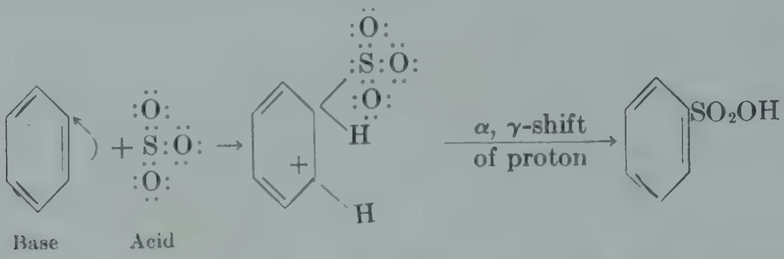
$$>C{=}O + \overset{+}{H} + \overset{-}{X} \rightleftarrows >C{=}O\begin{smallmatrix}H \\ X\end{smallmatrix}$$

or, more specifically,



$$\underset{\displaystyle OH}{R\cdot C}{=}\overset{\pm}{O} + \overset{+}{H} + HS\overset{-}{O_4}{}^{-} \rightleftarrows \underset{\displaystyle OH}{R\cdot C}{=}O\begin{smallmatrix}H \\ O(SO_2)OH\end{smallmatrix}$$

In the sulfonation of aromatic hydrocarbons, addition may take place by means of unsatisfied carbon valences of the benzene ring, and the mechanism of reaction can be explained by the electronic theory of acids and bases. According to this theory, acids such as SO_3, H_2SO_4, BF_3, $AlCl_3$, etc., are electrophylic agents (electron acceptors) and form a coordinate bond with a base (electrodotic agent) by accepting a share in an electron pair.[1] The sulfonation of benzene by sulfur trioxide may be represented as involving the formation of an addition compound having a coordinate bond, which is followed by a shift of the proton from the ring to an oxygen atom of the sulfonic acid group.



It is known that the rate of sulfonation increases with increasing acid concentration in sulfuric acid of less than 100 per cent concentration and with the concentration of sulfur trioxide in oleum. The behavior of acids as electron acceptors probably explains the utility of HF, BF_3, $AlCl_3$, and H_2SO_4 as catalysts for Friedel–Crafts' and similar alkylation reactions.

VI. TECHNICAL METHODS OF SULFONATION

Substances sulfonated by sulfuric acid, oleum, etc., can be divided into two general classes: (1) those which can be volatilized, *e.g.*, benzene, naphthalene, etc., and (2) those which cannot be easily vaporized, *e.g.*, α-nitronaphthalene and anthraquinone. Usually, the material being sulfonated is in the liquid phase at the temperature of sulfonation, but there are some exceptions. The substances of both classes can be sulfonated by the batch method, but only those of the first class lend themselves advantageously to the process of continuous sulfonation.

Batch Sulfonations. *Introducing Reactants.*—In batch or discontinuous sulfonation, the introduction of the reactants into the sulfonator varies with the physical and chemical properties of the materials undergoing treatment. It is customary to add anthraquinone compounds to fuming sulfuric acid, but concentrated sulfuric acid is generally added to the more volatile benzene. In sulfonating naphthalene, the aromatic hydrocarbon is generally melted in the kettle prior to the introduction of acid, although a number of operators prefer to introduce the reactants alternately in regulated portions.

Removing Water of Reaction.—From a study of the relationship between SO_3 concentration and sulfonation activity, it is apparent that unless a method is devised to prevent excessive dilution because of water formed during the reaction, the rate of sulfonation will undergo gradual deceleration. Finally, the reaction will be stopped at a definite H_2SO_4

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[1] Luder and Zuffanti, *Chem. Rev.*, **34,** 348 (1944).

or SO_3 concentration—different for each organic compound undergoing sulfonation. With respect to economy in sulfuric acid consumption, it is advantageous physically to remove or chemically combine this water, and various methods have been devised for accomplishing this purpose.

Use of Oleum.—The use of oleum for maintaining the necessary SO_3 concentration of a sulfonation mixture is a practical procedure that can be employed for the disulfonation of benzene and naphthalene. Preferably, the oleum and organic compound should be added gradually and concurrently to a large volume of cycle acid so as to take up the water as rapidly as it is formed by the reaction.

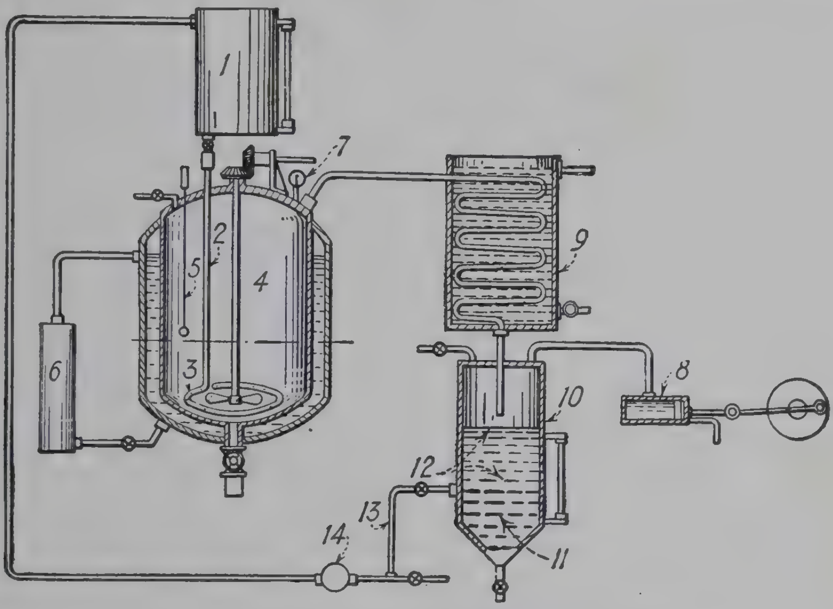
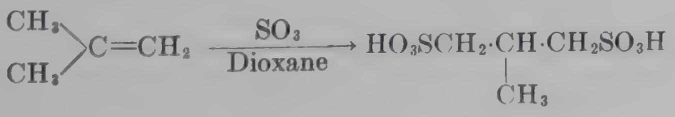


Fig. 14.—Apparatus for the sulfonation of benzene.

1. Benzene supply.
2. Benzene feed line.
3. Perforated distributor for benzene
4. Sulfonator.
5. Thermometer.
6. Oil heating mechanism.
7. Pressure gauge.
8. Vacuum pump.
9. Cooling coil.
10. Condensed liquor tank.
11–12. Water and benzene layers, respectively.
13. Recovered benzene-return line.
14. Circulating pump.

Use of Sulfur Trioxide Addition Compounds.—Sulfur trioxide addition compounds have been found to be particularly useful for the sulfonation of aliphatic hydrocarbons derived from the cracking of petroleum. Isobutylene is thus sulfonated by the use of sulfur trioxide and dioxane in ethylene dichloride at 0° to yield 2-methylpropane-1, 3-disulfonic acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH_2 \xrightarrow[\text{Dioxane}]{SO_3} HO_3SCH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2SO_3H$$

These sulfonic acids are usually converted to esters that have good detergent qualities.

Sulfur trioxide and sodium nitrite form addition compounds that are particularly useful for the sulfation (esterification) of the higher molecular-weight, unsaturated, fatty alcohols, such as oleyl alcohol, to yield the oleyl alcohol sulfates.[1] It is to be observed that the olefinic linkage is not affected by this sulfation process.

Use of Vacuum.—The use of reduced pressure for removing the water of reaction has some technical advantages in the sulfonation of phenol[2] and of benzene.[3] According to Downs, the disulfonation of benzene may be carried out under an absolute pressure of 0.5 to 1.0 in. of mercury at 260°C., with a lower ratio of oleum than is otherwise feasible. Under such conditions, sulfuric acid itself can be distilled from the reaction mass. Bender produced benzenesulfonic acid in the apparatus shown in Fig. 14 by carrying out the sulfonation in the ordinary manner to obtain the maximum absorption of benzene in sulfuric acid and then removing the excess of benzene and water under reduced pressures at 150 to 180°C. to reduce the ratio of water to sulfuric acid at the close of the reaction to less than 22:78.

Partial-pressure Distillation.—The use of the partial-pressure method is predicated upon the ability of the diluent to remove the water of reaction as it is formed and, hence, maintain a high concentration of sulfuric acid. If this concentration is maintained, the necessity for using excess sulfuric acid is eliminated, since its only function in ordinary sulfonations is to keep the desired high acid concentration.

The production of sulfanilic acid in a partial-pressure system has been shown to be feasible on a small scale, kerosene being used as the diluent. The yields are improved with increased ratios of diluent and temperature. When stoichiometric quantities of aniline and sulfuric acid (93 per cent) are used, yields of 95 per cent sulfanilic acid have been obtained.[4]

Special Sulfonating Processes: Discontinuous. *Guyot or Tyrer Process.*[5,6]—Here advantage is taken of the low boiling point of some aromatic hydrocarbons to remove the water formed during sulfonation. The method is applicable to compounds boiling below 200°C. Benzene may accordingly be sulfonated as follows: Sulfuric acid of 90 to 92 per cent strength is heated to 95 to 110°C. in a closed vessel, and benzene vapors from a special boiler are introduced into the heated acid through a pipe extending below a perforated cast-iron plate located in the bottom of the sulfonator. Provision is made for the condensation of the vapors

[1] Wolter, U. S. 2,231,979 (1941).

[2] Hazard-Flamand, Ger., 141,751 (1903).

[3] Downs, U. S. 1,279,295 (1918). 1,301,785 (1919); Bender, U. S. 1,301,360 (1919).

[4] Jacobs, Othmer, and Hokanson, *Ind. Eng. Chem.*, **35**, 321 (1943).

[5] Tyrer U. S. 1,210,725 (1917); Guyot, *Chimie & industrie*, **2**, 879 (1919).

[6] Maquire and Gould, U. S. 2,379,585 (1945).

emerging from the kettle and for the separation of the benzene and aqueous layers, the benzene being returned in vapor form to the sulfonator (see Fig. 14). Benzene vapor is passed into the sulfuric acid at a rate of not greater than 1.25 parts by weight of benzene per hour per part of acid, preferably at rate of between 0.6 and 1.0 part benzene at the beginning of the operation. The temperature of the acid is kept at 85 to 110°C. at the start, then increased to about 180°C., and finally reduced to 140 to 165°C. to complete the reaction. The time taken to reach 180° may vary somewhat, depending upon the rate of flow of benzene vapor and concentration and initial temperature of the acid. Up to 97 per cent of the sulfuric acid can be used up in this process. The advantage in closely controlling the variable conditions lies in low sulfone and disulfonic acid formations.

This process can be employed with volatile organic compounds such as toluene, xylenes, and chlorobenzene, which are capable of being sulfonated directly by sulfuric acid not containing free sulfur trioxide.

Instead of benzene vapors being passed into the heated sulfuric acid, liquid benzene under pressure can be introduced. The vapors leaving the system are passed through a water separator, and the condensed benzene is automatically and continuously returned to the system.[1] As operations are conducted at 130 to 135°C. with 100 per cent H_2SO_4, only 3.05 per cent of the acid remains after 8 hr. A typical analysis of a sample taken when the sulfuric acid content is reduced to 4.0 to 4.5 per cent is as follows:

$C_6H_5{\cdot}SO_3H$	93 –94%
H_2SO_4	4.0– 4.5%
H_2O	1.5– 2.0%
$(C_6H_5)_2SO_2$	0.5%

Gay, Aumeras, and Mion Process.[2]—The Guyot process cannot be used successfully with naphthalene, because a temperature in excess of 200°C. is required to remove the water of reaction, and this condition results in a charred sulfonic acid. The liberated water may, however, be removed by the use of an auxiliary liquid (*i.e.*, partial-pressure distillation) or an inert gas. The auxiliary liquids, such as carbon tetrachloride or ligroin, are characterized by the fact that their vapors are practically insoluble in the reaction mixture at sulfonation temperatures. These liquids, when circulated through the charge at 170°C., remove the water of reaction. The condensed vapors are subsequently separated, and the auxiliary liquid returned to the sulfonator.

Continuous Sulfonation. *Dennis and Bull Process.*—A process for the continuous sulfonation of aromatic hydrocarbons is based on the discovery by Dennis that although the solubility of pure benzenesulfonic acid in benzene is negligible, in the presence of free sulfuric acid, benzene will take up between 2 and 3 per cent of its own volume of the sulfonic acid.[1] Bull applied this principle in the technical sulfonation of benzene, the salient features of the procedure being shown in Fig. 15.[2]

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[1] Zakharov, *J. Chem. Ind.* (*Moscow*), **6**, 1648 (1929).

[2] Gay, Aumeras, and Mion, *Chimie & industrie*, **19**, 387 (1928).

The vessels (6 to 10) are filled with benzene through the pipe 17. Sulfuric acid or preferably oleum is then introduced into the upper reaction vessel through the pipe 11. Owing to its greater density, the acid flows downward through the series of reactors and comes into intimate contact with the ascending aromatic hydrocarbon. Because of the large excess of benzene used, the benzenesulfonic acid is extracted and leaves the system by the top outlet 22 as a 2 per cent solution. The residual sulfuric acid of approximately 77 per cent H_2SO_4 leaves the system at the lower outlet pipe 16 and is then concentrated for reuse.[3] It is also feasible to circulate the spent acid through a SO_3 absorption system and thus effect its concentration.

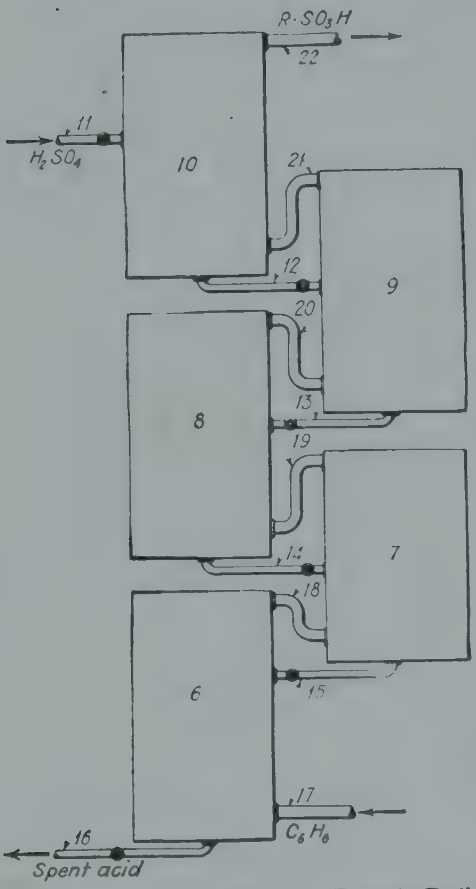

Fig. 15.—Plant assembly. Dennis-Bull process for the sulfonation of benzene.

The benzene-benzenesulfonic acid mixture may be sent to washers to remove the sulfonic acid and liberate the benzene. The aqueous solution of the acid then may be utilized to neutralize the sodium phenoxide produced by alkali fusion of the sodium benzenesulfonate, thus providing an economical procedure for the preparation of phenol.

VII. DESIGN AND CONSTRUCTION OF APPARATUS

Cast-iron apparatus is suitable for sulfonations with concentrated sulfuric acid of 88 to 98 per cent strength. When oleum or when mixtures containing free SO_3 are used, it is advisable to employ steel equipment. It is known that sulfur trioxide sometimes causes faults to develop in castings, and this is attributed to the action of the acid anhydride on the slag left in the pores of the cast iron.

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[1] Dennis, U. S. 1,211,923; 1,212,612 (1917).

[2] Bull. U. S. 1,247,499 (1917).

[3] Peterkin, *Chem. Met. Eng.*, **19**, 255 (1918).

Sulfuric acid (85 per cent, which is too weak for most sulfonations) has a specific conductance of only 0.1, and the value of the specific conductance of pure sulfuric acid is practically zero. Whereas dilute sulfuric acid, which is appreciably dissociated into $2\overset{+}{H}$ and $\overset{=}{SO_4}$, attacks iron, forming ferrous sulfate, sulfuric acid stronger than the dihydrate $SO_3 \cdot 2H_2O$ (85 per cent H_2SO_4) does not appreciably attack the iron vessels that are employed in synthetical processes.

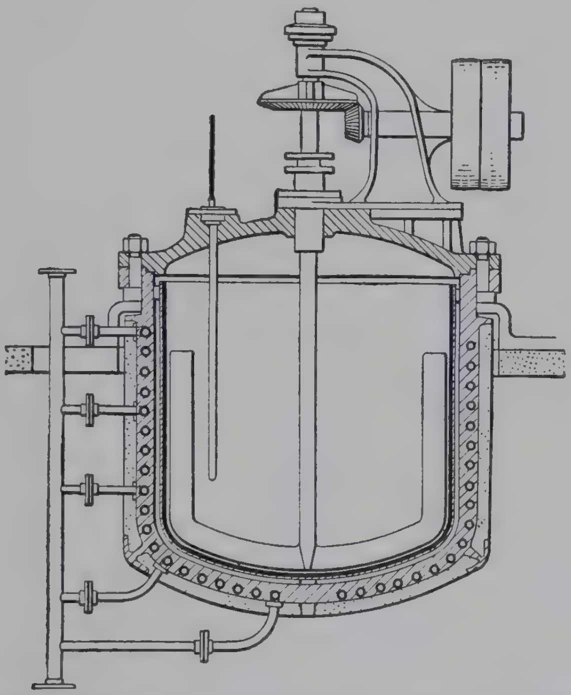

FIG. 16.—Sulfonator fitted for heating with hot water or low-pressure steam (Frederking system).

Valves and pumps fabricated from stainless steel (Type 316; Fe, Cr, 16–18; Ni, 10–14; C, 0–0.1; Mo, 2–3) have been found to be satisfactory for *unit operations* involving sulfuric acid. Pumps made of Duriron, Worthite, and Durimet are widely used for transferring sulfuric acid.

When the sulfonation involves no special characteristics such as have been discussed previously, the operation can be carried out conveniently in most of the available commercial vessels designed for this unit process. Typical industrial apparatus is shown in Fig. 16. Two factors are of importance in the design and construction of sulfonators, *viz.*, heat transfer and agitation. Although the problem of dissipating the heat of reaction is not so important as in nitration, operations at distinctly higher temperatures (200 to 280°C.) are necessary for certain sulfonations.

Consideration must also be given to the stirring of viscous mixtures in order to avoid surface overheating.

Heat Transfer.—Although sulfonation is an exothermal reaction, heat is frequently desirable to accelerate the initial reaction, and generally it is necessary to continue the heating during the final stages. Sulfonators are consequently provided with devices for effecting heat transfer, and these may be classified broadly as (1) jacket; (2) coils imbedded in castings (Thermocoil and Frederking construction); and (3) vertical cast-iron tubes. Obviously, a combination of the preceding methods may oftentimes be employed advantageously.

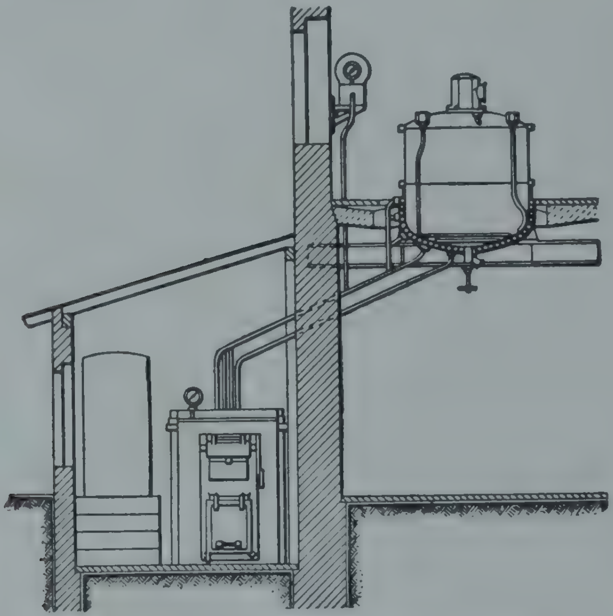

Fig. 17.—Thermocoil hot-water system.

A typical installation. Hot water, under pressure, circulates without pump or other mechanical device and, once properly adjusted, requires no attention other than to the furnace or heater.

Heating Agents.—Hot water, steam, heated oils, and hot gases find employment in sulfonation operations. Hot water automatically controlled at the desired temperatures oftentimes provide a satisfactory method of heating. In the Frederking or Thermocoil apparatus (Figs. 16, 17), the hot water or steam can be circulated under high pressures, and this makes possible obtaining relatively high temperatures, *i.e.*, 170 to 300°C. (Fig. 18). Steam is generally the most economical and efficient and therefore the most common means of heating a jacketed kettle. When high temperatures are required, steam is not generally employed in jacketed vessels because of the accompanying high pressures.

Heating by the use of hot oil or chemicals (Dowtherm) is frequently resorted to for operations requiring a temperature range of 200 to 250°C. The heat transfer agent is generally heated in a separate boiler and pumped to the jacket of the reactor. The rate of flow to the jacket is regulated automatically. It has the advantage over steam in that no great jacket pressures are involved but suffers in comparison since heat conduction through an oil film is considerably less than from a condensing vapor. Consequently, thermal efficiency must be sacrificed for the advantage gained in apparatus construction.

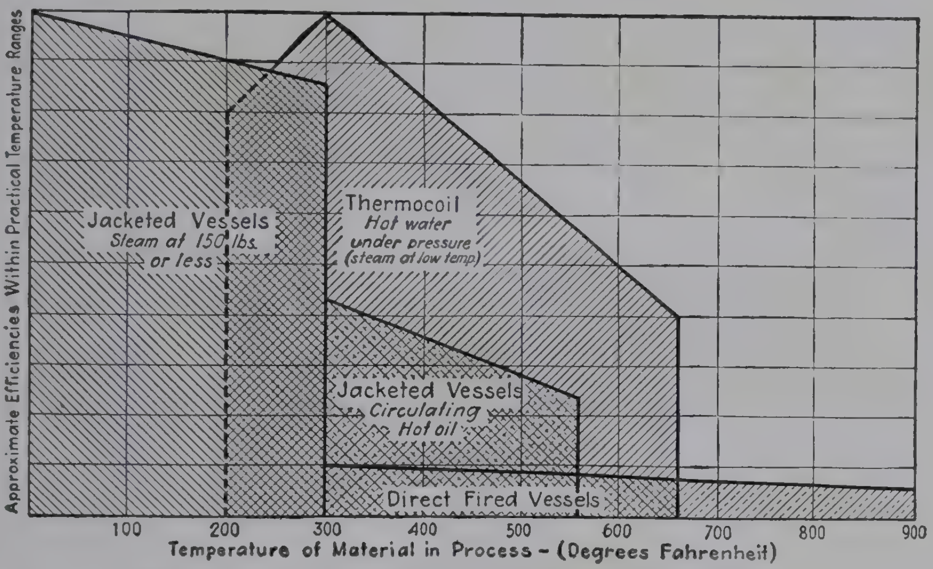

FIG. 18.—Thermal classification of processing systems.

VIII. TECHNICAL PREPARATION OF SULFONIC ACIDS

Sources of Loss.—In sulfonation operations, there are several known sources of loss, some of which can be determined analytically. These are (1) tar formation; (2) sulfone formation; (3) unreacted crude material; (4) undesirable sulfonic acids; (5) solubility losses in mother liquors; and (6) mechanical losses. Wherever possible, these sources of loss should be checked regularly, and methods devised to control such losses to the lowest possible limits. These losses may be illustrated by considering the sulfonation of naphthalene to naphthalene-2-sulfonic acid. It is known that (1) is small (less than 1 per cent); (2) can be limited to 0.5 to 1.0 per cent; (3) can be limited to less than 1.0 per cent; (4) and (5) amount to about 15 to 20 per cent; and (6) should be less than 0.5 per cent and varies with each sulfonation. It comprises sulfonic acid lost in discarded press cakes, spilling, etc.

Benzenesulfonic Acid.—For the production of benzenesulfonic acid, the sulfonator should be equipped with an efficient propeller and a reflux condenser. The operation is started by running 1,000 lb. of benzene into the sulfonator. Then, during a period of 6 to 8 hr., 2,050 lb. of 5 per cent oleum is delivered, and the temperature controlled at 35 to 40°C. by means of circulating water. After all the oleum has been added, the water is drained from the jacket and the temperature brought up to

100 to 110°C. by jacket steam. The unreacted benzene starts to reflux as the temperature is raised, and the reaction is complete in 2 to 3 hr. A sample of the sulfonation mixture is diluted with water to determine the presence of free benzene; and, if the reaction is incomplete, additional concentrated sulfuric acid is introduced, and the process continued.

The sulfonated mass may be treated by diverse methods. A simple procedure is to run the charge into 4,000 lb. of water, neutralizing with hydrated lime and then filtering the calcium benzenesulfonate from the gypsum. The sodium salt is obtained by boiling the solution of the calcium salt with soda ash and filtering to remove the calcium carbonate.

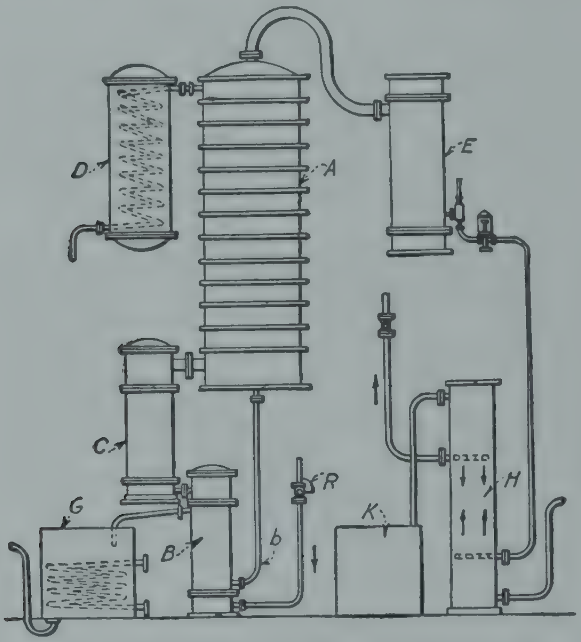

FIG. 19.—Sulfonation of benzene: Barbet process.

A. Reaction column.
B. Heat exchanger to preheat benzene.
b. Hot benzenesulfonic acid line.
C. Benzene vaporizer.
D. H_2SO_4 inlet.
E. Cooler for water vapors.
G. Outlet for benzenesulfonic acid.
H. Scrubber.
K. Reservoir for unsulfonatable volatile hydrocarbons.
R. Benzene inlet.

The solution of sodium benzenesulfonate may be evaporated or employed directly in subsequent reactions.

When the benzenesulfonic acid is to be employed in the synthesis of phenol, the sodium salt can be made by the addition of by-product sodium sulfite, which is obtained from the subsequent caustic fusion operations. The sulfite is put into solution with any available wash waters containing sodium benzenesulfonate, and the charge containing benzenesulfonic acid is then slowly introduced. The sulfur dioxide that is liberated is delivered to another vessel or absorption tower containing sodium phenoxide, thus accomplishing the useful purpose of liberating the phenol. The last traces of sulfur dioxide are removed by boiling with live steam. This economic utilization of materials is similar to the method of preparing β-naphthylamine from sodium β-naphthalenesulfonate.[1]

Continuous Sulfonation of Benzene.—The sulfonation of benzene can also be carried out continuously and economically by the method of Barbet.[2]

The process is carried out as follows:[3] Sulfuric acid of 98 per cent strength is heated in the coil *D* (Fig. 19) and delivered to the top of a cast-iron reaction tower *A*, which is provided with baffle plates and a suitable stoneware packing. By means of heat provided by steam coils located on the baffles, a temperature of 150°C. is maintained within the tower. Benzene is heated in the heat exchanger *B* by the descending benzenesulfonic acid and is vaporized in the vessel *C*. The benzene vapors enter at the bottom of the reaction tower and, on ascending, come in contact and react with sulfuric acid of increasing strength. The hydrocarbon is finally completely converted to benzenesulfonic acid, which, with the excess of mineral acid, flows out at the base and passes through the heat exchanger.

Water and acid vapors as well as other gaseous impurities will pass to the cooler *E* and then to the scrubber *H*, where the sulfurous acid is removed by washing. The benzenesulfonic acid may be worked up according to the procedures previously described or may be used to neutralize a solution of sodium phenoxide,[4] thus producing phenol and sodium benzenesulfonate.

Benzene-1, 3-disulfonic Acid.—The calcium salt of benzenesulfonic acid may be used for the preparation of the disulfonic acid. Because of the high temperatures and heavy load, it is necessary to employ a Thermocoil system or heat with circulating oil and to use an efficient stirrer. In this process, 1,670 lb. of powdered anhydrous calcium benzenesulfonate and 1.25 lb. of sodium carbonate (to prevent formation of lumps) are added to 2,600 lb. of 95 per cent sulfuric acid at 200°C. in a cast-iron sulfonator. The temperature is raised to 250°C. over a period of 6 hr. and held at this point for 1 hr. The batch is then dropped into 800 gal. of water and neutralized by the addition of milk of lime. The suspension is heated to boiling with live steam and filtered from the gypsum. The calcium benzenedisulfonate is converted to the sodium salt by treating with a hot solution of sodium carbonate.

The disulfonic acid may be prepared at much lower temperatures, *e.g.*, 70 to 120°C., and with greater economy with respect to the sulfuric acid by using a cyclic system of sulfonation. Here the concentrated sulfuric acid that is present at the termination of disulfonation (cycle acid) is used to prepare the monosulfonic acid. The process may be carried out as follows:[1]

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[1] Campbell, *J. Soc. Dyers Colourists*, **38**, 114 (1922).

[2] Barbet, U. S. 1,459,081 (1923).

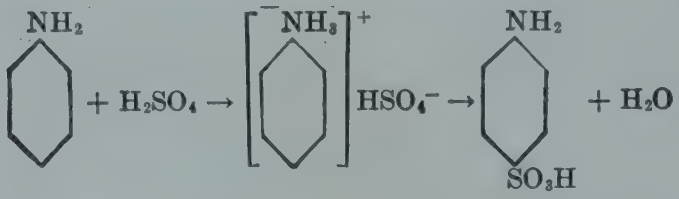
[3] This process was developed independently at the Color Laboratory by Ambler and Gibbs [U. S. 1,300,228 (1919)].

[4] Dennis, U. S. 1,227,894 (1917).

Monosulfonation.—Into a mixture of 213.6 parts of sulfuric acid-monohydrate (approximately 2 moles) and 476 parts of benzene disulfonic acid (2 moles), there is added gradually over a period of about 4 to 5 hr. 78 parts (1 mole) of benzene. The temperature, which is kept at about 70°C. during the feeding operations, is raised to 120°C. and maintained at that point for about 1 hr. During this phase of the operation, the residual acid resulting from disulfonation is used for the monosulfonation of benzene.

Disulfonation.—The charge is cooled to 70°C., and 286 parts of 60 per cent oleum (containing 2 moles SO_3 and 1.09 moles of sulfuric acid) is run in over a period of 4 hr. Toward the end of this operation, the temperature is permitted to rise to 100°C. and is then further raised to 120°C. within a period of about ½ hr. After this temperature has been maintained for 3 hr., disulfonation is substantially complete. One-third of the charge is then removed for treatment with lime. The residue—which is identical with the cycle acid used at the beginning of the operation—is cooled to 70°C., and the operation is repeated.

Sulfanilic Acid. *Preparation by Baking Process.*



The contents of one drum of aniline, *i.e.*, about 900 lb., are emptied into a shallow mixing pot or mixing machine, which preferably is made of an acid-resistant alloy; 1,050 lb. of 66°Bé. (93.2 per cent) of water-white sulfuric acid is then fed in very slowly, with constant and thorough agitation. A thick paste is obtained, which is removed while warm and placed in trays in a vacuum oven. Heat is supplied to the oven by superheated steam or a circulating oil system.

The paste is heated at 200°C. for 6 hr. The dry cake is discharged into a lead-lined mixing kettle provided with a cover and vent. The material is now slightly gray in color and is upward of 90 per cent pure. In this crude form, it contains from 0.3 to 3.0 per cent unchanged aniline and some carbonaceous impurities. The "bake" is put into solution with dilute sodium carbonate, precaution being taken to ensure a strong blue coloration with litmus. Live steam is then passed into the charge to remove all traces of aniline. Some decolorizing carbon is added, and the solution passed through a pressure filter. The filtrate is suitable for making certain azo dyes and in some plants is thus employed The sodium salt is often made by treating the crude sulfanilic acid with milk of lime, reacting the calcium salt with sodium carbonate, and then filtering to remove the calcium carbonate. When this solution is acidified with sulfuric acid, a good quality of free acid is obtained. The purified material is put on a filter, washed, and then dried in a vacuum oven. The yield of purified sulfanilic acid should be over 90 per cent of theory or in excess of 165 lb. based on 100 lb. of aniline used.[1]

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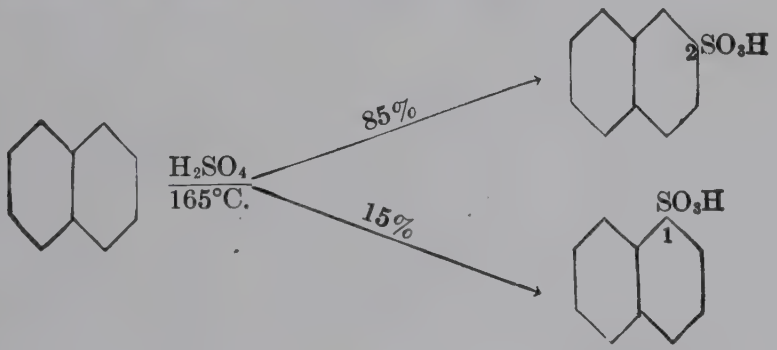
[1] U. S. 1,956,571 (1934).

Naphthalene-2-sulfonic Acid.



When naphthalene is sulfonated at 165°C., the principal product is naphthalene-2-sulfonic acid, and about 15 per cent of the alpha isomer is formed simultaneously. Of powdered naphthalene, 5,000 lb. is charged into a jacketed cast-iron sulfonation kettle, melted, and heated to 165°C. Then 5,400 lb. of 98 per cent sulfuric acid is run into the molten naphthalene at such a rate that the temperature does not rise above 165°C. This takes about 3 hr. The heating and stirring are continued for an additional hour, and the reaction mass is then dropped into 1,760 gal. of water contained in a lead-lined vat, fitted with a stirrer. The batch is neutralized with milk of lime at the boiling temperature. The volume at the end of this operation should be about 5,630 gal. The calcium naphthalene-2-sulfonate in solution is filtered from the gypsum and cooled to 20°C. in a tank provided with cooling coils. The calcium salt of the acid crystallizes out and is separated by filtration from the alpha isomer and disulfonates that are in the mother liquor. The calcium salt may be converted to the sodium salt by treatment with a solution of soda ash. The sodium salt may be made directly by completely neutralizing the sulfonation charge with soda ash, adding sufficient sodium chloride to give a solution of 17°Bé., and allowing to crystallize overnight.

The product may be tested for completeness of sulfonation by distilling with steam. A typical analysis reveals the presence of 0.6 per cent free naphthalene and 0.9 per cent sulfone. The latter remains in suspension in the acid solution and may be removed by filtration. The percentage of alpha isomer may be determined by converting the dried calcium salts to the sulfonchlorides with phosphorus pentachloride and estimating the components from melting point-composition curves, the melting point of the alpha and beta derivatives being 67 and 77°C., respectively.

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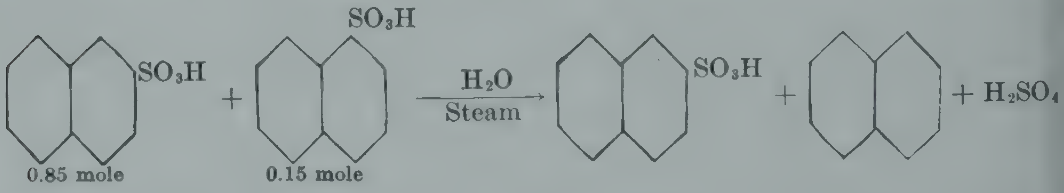
[1] HUBER, *Helvetica Chim. Acta*, **15**, 1372 (1932).

Naphthalene-2-sulfonic Acid: Alternative Procedure.—The preparation of β-naphthalenesulfonic acid with respect to its utilization in the manufacture of β-naphthol is advantageously carried out as follows:[1] 3,350 lb. of naphthalene is charged into a 1,500-gal. sulfonator, and the hydrocarbon melted by warming to 90°C. With rapid agitation, 3,350 lb. of sulfuric acid (93.0 per cent) is run in, the temperature being permitted to rise to 160°C. The charge is heated at 160 to 165°C. for several hours. During this period, some of the naphthalene distills off and is cooled in condensers kept at 90°C. by means of hot water. The naphthalene thus condensed and recovered is subsequently dried and reused.

The reaction product contains 85 per cent of the β-sulfonic acid and 15 per cent of the alpha isomer. The latter is now removed by blowing dry steam into the charge whereby the naphthalene-1-sulfonic acid is desulfonated (hydrolyzed) and the liberated naphthalene is distilled off and recovered. It is essential to employ dry steam to avoid foaming, and to maintain a temperature of 160 to 165°C. to expedite the hydrolytic reaction. About 18 per cent, or 542 lb. of the original naphthalene employed, is recovered, leaving the residual β-naphthalenesulfonic acid contaminated with about 0.1 per cent alpha isomer.



The "hydrolyzed" sulfonation mixture is discharged into 1,600 gal. of water (13,400 lb., or 4 lb. of water per pound of naphthalene originally used) under vigorous agitation. This diluted solution is then run into a previously prepared solution of 4,750 lb. of salt in 14,100 lb. of water (1,750 gal. of solution), whereby the formation of the sodium-2-naphthalenesulfonate is effected. The mixture is agitated for a period of about 10 hr. or until the charge has cooled to 30°C. and is then filtered.

The filtration is accomplished by pumping or blowing the sodium sulfonate suspension into a pressure filter containing wooden plate filters and rubber-coated frames. The shell of the filter is coated with tar to minimize corrosion. The filtrate is permitted to stand and more salt added if necessary and then refiltered to collect any additional sulfonate that has crystallized out. The second crop of sodium sulfonate is not so pure as the first. The filter cakes are generally washed with a minimum of water, and these washings are employed to advantage as part of the liquor in the sulfonation dilution tank.

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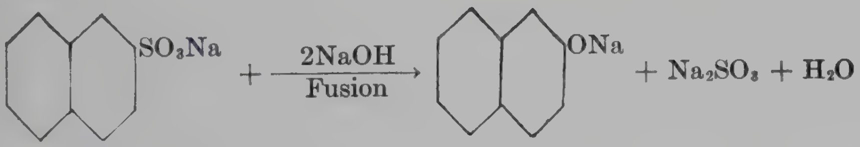
[1] Shreve, *Color Trade J. Textile Chem.*, **14**, 42 (1924); *cf.* U. S. 1,922,813 (1933), which is practically identical.

The filter cake of sodium naphthalene-2-sulfonate containing about 70 per cent of water is packed into the trays of hydraulic presses and subjected to pressure until the water content is approximately 30 per cent. The press cakes are disintegrated and then delivered to the fusion kettles for the preparation of β-naphthol.



When the naphthalenesulfonic acid is to be converted to β-naphthol, the sulfonic acid may be treated with the alkali fusion mass obtained in the ensuing operation. The reactions that take place are as follows:

$$C_{10}H_7SO_3Na + 2NaOH(\text{Fusion}) \rightarrow C_{10}H_7ONa + Na_2SO_3 + H_2O \quad \text{(I)}$$

$$C_{10}H_7ONa + C_{10}H_7SO_3H \rightarrow C_{10}H_7OH + C_{10}H_7SO_3Na \quad \text{(II)}$$

Preparation of 2-Naphthol-1-sulfonic Acid. *Sulfonation with Chlorosulfonic Acid.*—Chlorosulfonic acid is employed to sulfonate β-naphthol when the 1-sulfonic acid is desired. The sulfonation is carried out in a jacketed cast-iron vessel provided with a brine coil and a propeller stirrer. The liberated hydrogen chloride escapes through a vent and is advantageously absorbed in water.

The reactor is charged with 500 lb. of *o*-nitrotoluene and 144 lb. of β-naphthol. The solution obtained is cooled to 0°C., and 140 lb. of chlorosulfonic acid is then run in at such a rate that the addition of acid requires about 3 hr. The charge is stirred for 3 hr. longer, the temperature being maintained below 10°C.

When hydrogen chloride ceases to be liberated, the reaction mass is dropped into a conical wooden tank containing 2,200 lb. of water, whereupon the *o*-nitrotoluene separates and the 2-naphthol-1-sulfonic acid is dissolved in the water. The nitrotoluene is drawn off, and the aqueous solution neutralized with potassium carbonate. The potassium salt of 2-naphthol-1-sulfonic acid is salted out with potassium chloride and is then filtered off.

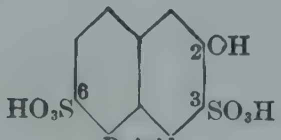
Preparation of 1-Amino-2-naphthol-4-sulfonic Acid. *Sulfonation with Sodium Bisulfite.*—In the preparation of 1-amino-2-naphthol-4-sulfonic acid, 1,000 lb. of water, 28 lb. of caustic soda, and 100 lb. of β-naphthol are charged into a wooden tank provided with a wooden stirrer. A solution of 50 lb. of sodium nitrite (96 per cent) dissolved in 1,000 lb. of water is then added. About 1,000 lb. of crushed ice is added to reduce the temperature to 0 to 5°C., whereupon a mixture of 1,260 lb. of water, 1,000 lb. of ice, and 140 lb. of sulfuric acid (98 per cent) is added. After stirring for 2 hr., the mixture is filtered and the press cake is washed with a moderate amount of water. The nitrosonaphthol is obtained in the form of a cake containing about 80 per cent water.

The wet nitrosonaphthol from the preceding operation is mixed in another wooden tub with 1,500 lb. of water and 206 lb. of sodium bisulfite. The nitrosonaphthol dissolves; and, when solution is complete, the charge is filtered into another tank. The clear solution is heated to 40°C., and 230 lb. of hydrochloric acid run in. The mixture is then kept at 40°C. overnight while stirring. The 1-amino-2-naphthol-4-sulfonic acid separates out as a pinkish flaky solid which is easily filtered and washed. The yield of sulfonic acid is about 235 lb. of moist or 112 lb. of dry product, equivalent to 77 per cent of theory.

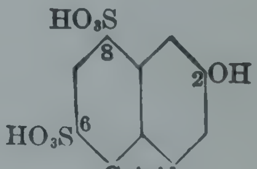
Sulfonation of β-Naphthol.—When β-naphthol is sulfonated at 100°C. with 98 per cent sulfuric acid, 2-naphthol-6-sulfonic acid (Schäffer acid) is obtained as the principal product. 2-Naphthol-3, 6-disulfonic acid (R acid) is also formed to the extent of 20 to 30 per cent, and this is found in the mother liquor after separating the monosulfonate.

To prepare the monosulfonic acid, 144 parts of powdered naphthol is added to 216 parts of 98 per cent sulfuric acid at 60°C. The temperature is then raised to 100 to 105°C. and thus maintained for 2.5 hr. or until a sample dissolves completely in water. The charge is then run into 1,000 parts of water, and 200 parts of salt is added. Upon cooling, with stirring, the Schäffer salt separates out practically completely during the course of a day. It is filtered off and washed with a minimum of brine. About 200 parts of product averaging 75 per cent pure Schäffer salt is thus obtained. This corresponds to a yield of approximately 67 per cent based on the quantity of monosulfonate theoretically possible. The mother liquor is treated with sodium sulfate and evaporated to precipitate out the disulfonate, R salt.

The Disulfonic Acids of 2-Naphthol.



R Acid



G Acid

When 2-naphthol is sulfonated with an excess of sulfuric acid, both 3, 6- and 6, 8-disulfonic acids (R and G acids), respectively, are produced at all temperatures and with all acid concentrations. At temperatures below 100°C., G acid is preponderant; above 100°C., the quantity of R acid increases with an increase in operating temperature until, at 160°C., it is the principal constituent in the sulfonation mass.

The sulfonator is charged with 720 lb. of 98 per cent sulfuric acid, and 144 lb. of β-naphthol is added. The charge is kept at 50°C. for 50 to 60 hr. until the decrease in acidity indicates that disulfonation has taken place. The reaction mass is dropped into water, treated with hydrated lime, and filtered hot from the precipitated gypsum. The calcium salt may be converted to the potassium salt by treatment with potassium sulfate and filtering. The solution is evaporated and acidified with hydrochloric acid; and on cooling, the G acid, *i.e.*, 2-naphthol-6, 8-disulfonic acid, separates out as a technically pure product. After standing 1 to 2 days, it is filtered and washed with a potassium chloride solution. The filtrate and washings, on evaporation, yield R acid.

Anthraquinonesulfonic Acids. *Preparation of Anthraquinone-2-sulfonic Acid.*—The sulfonation of anthraquinone is carried out in large steel vessels provided with an efficient stirrer and a jacket for heating. Technical anthraquinone, 2,400 lb. (purity 99 per cent), is added slowly to 2,500 lb. of 25 per cent fuming sulfuric acid at room temperature. The reaction mass is stirred thoroughly while the temperature is raised to 135°C. over a period of 1.5 hr. It is maintained at this temperature for 3 hr.; and during this period, 1,000 lb. of 40 per cent oleum is added. The charge is heated finally at 140°C. for 1 hr.

After cooling, the contents of the sulfonator are run into a large vat, lined with lead, which contains 2,000 gal. of cold water. Live steam is passed into the suspension until the unchanged anthraquinone becomes coarse grained and easy to filter. The charge is then filtered, and the retained anthraquinone is washed with water. The filtrate is always deep brown and contains the soluble, free acids.

The neutralization by lime, which is often suggested, is not satisfactory. All salts of anthraquinone-2-sulfonic acid are so moderately soluble (see Table VII) that they precipitate readily in strong acid solutions. Immense quantities of water would consequently be necessary to keep the calcium salt in solution.

Seven thousand pounds of sodium chloride is added to the warm filtrate, which is stirred while cooling. It is then permitted to stand for 10 hr. The sodium anthraquinone-2-sulfonate separates out as yellow mother-of-pearl leaves. It may be colored brown to gray according to the increased purity of the sulfonate. In the latter case, the pressed cake has the appearance of a silver bar—whence the popular synonym *silver salt*.

The sodium salt is filtered off and washed with a saline solution and when air dried contains a molecule of water of crystallization. The technical product employed in subsequent syntheses usually averages about 90 per cent in purity, the contaminants being principally water, inorganic salts, and small amounts (1 per cent) of disulfonates. If the mother liquor from 2,000 to 1,000 gal. is concentrated and then cooled, part of the isomeric sodium disulfonates separate out. These are filtered off and washed with a saturated salt solution; the mother liquor and washings are discarded. The yield of β-anthraquinonesulfonic acid by this method of operation fluctuates within narrow limits but on the whole closely checks laboratory data, as can be observed by a study of the following two tables, VI*A* and VI*B*:

TABLE VI*A*.—TECHNICAL SULFONATION OF ANTHRAQUINONE

	Yield	
	Products, %	Acids, %
2,400 lb. of anthraquinone sulfonated		
1,200 lb. of anthraquinone recovered	50	
1,400 lb. of anhydrous sodium salt	39.2	78.4
200 lb. of 2, 6- and 2, 7-disulfonates	4.1	8.3
Loss by solubility, etc	6.7	

The mother liquor and washings contain most of the 2, 7-disulfonate, since at 20°C. its sodium salt is about ten times more soluble than the 2, 6-isomer.

TABLE VI*B*.—SULFONATION OF ANTHRAQUINONE

Anthraquinone, 104 Gm.; SO_3 Introduced as 20 Per Cent Oleum. Time, 4 Hr.

Expt. No.	Temp., °C.	SO_3 % of theory	Anthraquinone recovered, %	β-monosulfonic acid, %	β-disulfonic acids, %	α-sulfonic acids, %
1	120	100	62.8	81.4	16.5	2.1
2	130	100	56.2	78.4	19.2	2.4
3	140	100	38.5	73.6	24.4	2.0
4	160	100	36.3	72.4	24.9	2.7
5	180	100	33.8	70.9	26.6	2.5
6	140	60	58.2	83.6	13.6	2.8
7[1]	140	80	49.6[1]	80.2[1]	17.3	2.5
8	140	120	34.4	70.6	27.3	2.1
9	140	150	34.0	66.4	30.7	2.9

[1] Compare with results in Table VI*A*.

With only slight modifications of the process and with complete precipitation of the sulfonic acids, Lauer obtained the data shown in Table VI*B*.[1]

Data relative to the solubility of salts of anthraquinonemonosulfonic acids are shown in the following table:

TABLE VII.—COMPARISON OF SOLUBILITY OF α- and β-ANTHRAQUINONEMONOSULFONIC ACIDS[1]

Cation	α-Anthraquinonemono-sulfonic acid		β-Anthraquinonemono-sulfonic acid	
	18°C.	100°C.	18°C.	100°C.
NH_4	1:60	Very soluble	1:20	1:2
K	1:100	1:25	1:110	1:10
Na	1:100	1:20	1:120	1:5
Mg	1:100	1:20	1:300	1:100
Ca	1:250	1:50	1:800	1:200
Sr	1:1,000	1:140	1:1,100	1:200
Ba	1:2,500	1:1,000	1:3,000	1:500

[1] According to ANDERAU, Diss. E.T.H., Zurich (1925).

Preparation of Anthraquinone-1-sulfonic Acid. *In the presence of a catalyst.*—When approximately 1 per cent of mercury as the sulfate or oxide is added to the oleum employed for sulfonation and the operation is conducted in a manner similar to that used previously, anthraquinone-1-sulfonic acid is the principal product obtained.

Two thousand eighty pounds of anthraquinone is triturated with 30 to 40 lb. of mercuric oxide or sulfate and then gradually delivered into 2,000 lb. of 20 per cent oleum. The temperature rises during the feeding operation to approximately 50°C., and, with the aid of external heat, this is brought up to 130 to 135°C. in a period of 1 hr. During the next 2 hr., 750 lb. of 40 per cent oleum is added, and the reaction completed by heating for an additional hour. The charge is cooled and run into 2,000 gal. of cold water, and, after heating with live steam, the coarse-grained unconverted anthraquinone is filtered off. The filtrate is light brown and contains the very soluble α-sulfonic acid, which is precipitated as the potassium salt by the addition of 1,000 lb. of potassium chloride to the boiling and thoroughly agitated solution. Since potassium anthraquinone-1-sulfonate separates out almost immediately, it is advantageous to add the potassium chloride as a hot solution. The suspension is cooled to 60°C. while stirring.

At this temperature, the 1, 5-disulfonate is very soluble compared with the monosulfonate; whereas at 18°C., both are sparingly soluble.

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[1] LAUER, *J. prakt. Chem.*, **135**, 166 (1932).

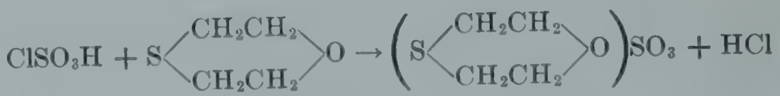
Adoption of this technic provides a simple way of obtaining the potassium anthraquinone-1-sulfonate with minimal quantities of disulfonic derivatives.

By recrystallization from hot water, the traces of the more soluble beta derivative that may be present in the principal alpha sulfonate are removed.

According to Lauer, it is best to adjust the operating conditions to obtain a conversion of 75 per cent of the anthraquinone employed.[1] Under such circumstances, the yield of α-monosulfonic acid is approximately 55 per cent, based on anthraquinone used or 70 per cent of that theoretically obtainable. These relationships are brought out by the data in Table V (page 306), which also show the effect of the type of mercury catalyst.

Sulfonation of 2-Pentene. *With Thioxane*—SO_3.—Sulfur trioxide, 40 parts by weight, is added to a mixture of 350 parts of carbon tetrachloride and 52 parts of thioxane while the reaction temperature is maintained at 30°. Then 35 parts of 2-pentene is added, and stirring is continued until all solids have disappeared. The reaction mixture is then permitted to separate into two layers, the upper viscous layer containing the 2-pentenesulfonic acid. Neutralization of the top layer with a caustic soda solution yields, on drying, 85 parts by weight of 2-pentene sodium sulfonate as a hygroscopic, glasslike material.[2]

Chlorosulfonic acid can be introduced instead of sulfur trioxide, and the operating conditions adjusted to produce a product that is more extensively sulfonated. Accordingly, 65 parts of chlorosulfonic acid is added to a mixture of 175 parts of ethylene dichloride and 52 parts of thioxane at room temperature.



$$ClSO_3H + S\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}O \rightarrow \left(S\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}O\right)SO_3 + HCl$$

The reaction mixture is heated to boiling under a reflux condenser to remove most of the hydrogen chloride. 2-Pentene, 17.5 parts, is added to the cooled mixture; the temperature then raised to 50 to 60°; and the mixture stirred for several hours until all solids are dissolved. The reaction mixture is neutralized with caustic soda solution at 10°. The neutral solution separates into two layers; the aqueous layer, which contains the dissolved sulfonates, yields, on drying, 88 parts of a white solid of the following composition: 2.6 per cent sodium chloride; 13.5 per cent sodium sulfate, and 83.9 per cent organic material, containing 21.6 per cent organically bound sulfur.

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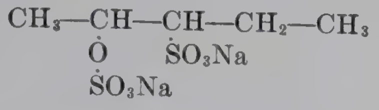
[1] Lauer, *J. prakt. Chem.*, **130,** 216 (1931).

[2] Nawiasky and Sprenger, U. S. 2,335,193 (1943).

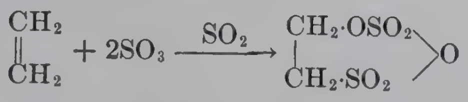
Inasmuch as 2-pentenesulfonic acid contains 18.6 per cent of combined sulfur, and a compound of the formula



$$CH_3{-}\underset{\substack{|\\ O\\ |\\ SO_3Na}}{CH}{-}\underset{\substack{|\\ SO_3Na}}{CH}{-}CH_2{-}CH_3$$

contains 21.9 per cent of organically bound sulfur, it appears that the product consists of compounds containing more than one sulfo group.

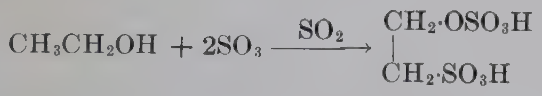
Preparation of Carbylsulfate and Ethionic Acid. *Carbylsulfate.*



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + 2SO_3 \xrightarrow{SO_2} \left.\begin{matrix}CH_2{\cdot}OSO_2\\ |\\ CH_2{\cdot}SO_2\end{matrix}\right\rangle O$$

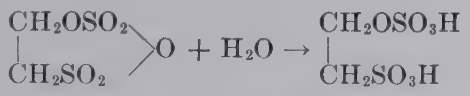
Two hundred forty parts of sulfur trioxide is dissolved in 480 parts of liquid sulfur dioxide. Into this solution, 28 parts of ethylene is introduced in a slow current. The SO_2 is eliminated by distillation, and the crystalline residue, after cooling to 0°C., is separated on a suction filter. Carbylsulfate is obtained in crystalline form in a yield of 90 per cent of theory.

Ethionic Acid.



$$CH_3CH_2OH + 2SO_3 \xrightarrow{SO_2} \begin{matrix}CH_2{\cdot}OSO_3H\\ |\\ CH_2{\cdot}SO_3H\end{matrix}$$

Ethyl alcohol (480 parts) is dissolved in 500 parts of liquid SO_2, which is instrumental in maintaining a low reaction temperature. Into this solution, there is run during a 6-hr. interval a mixture of 1,600 parts of SO_2 and 1,600 parts of SO_3. The reaction mass is stirred for about 10 hr. at 0°C. and then warmed to 10 to 15°C. to drive off most of the SO_2. The product consists of crude ethionic acid. Carbylsulfate also leads to ethionic acid by hydration in the cold.



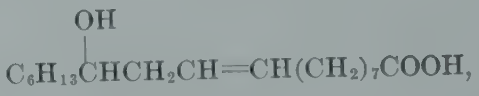
$$\left.\begin{matrix}CH_2OSO_2\\ |\\ CH_2SO_2\end{matrix}\right\rangle O + H_2O \rightarrow \begin{matrix}CH_2OSO_3H\\ |\\ CH_2SO_3H\end{matrix}$$

Sulfation of Fatty Alcohols. *With* SO_3-$NaNO_2$.—The addition compounds of SO_3 with sodium nitrite that are used in the following sulfonation are prepared by passing sulfur trioxide over pulverized sodium nitrite in a vacuum mixer containing a paddle scraper. Although the reaction is exothermic, it does not lead to the formation of nitric oxide. From 1 to 3 moles of sulfur trioxide can be coordinated with sodium nitrite, the ratio depending on the time of treatment and the relative quantities of reactants.

The SO_3-$NaNO_2$ addition compounds are particularly useful for the production of sulfates of the higher molecular-weight fatty alcohols. The preparation of the oleyl alcohol sulfate can be carried out as follows:[1]

One hundred and sixty-three parts of an addition product obtained from sulfur trioxide and sodium nitrite, containing 70 per cent of sulfur trioxide and corresponding to 1 mole of sodium nitrite to 2 moles of sulfur trioxide, is introduced in small quantities into a reaction chamber containing 350 parts of oleyl alcohol while the reaction mass is being stirred and cooled. During the introduction of the addition product, the temperature of the reaction mass is allowed to rise to 35°C., whereupon the temperature is slowly increased to 65°C. After a short period of stirring, the reaction goes to completion. Then the reaction product is neutralized with solid pulverized caustic soda or aqueous alkaline solutions. A high percentage yield of the sodium salt of oleyl alcohol sulfate is obtained immediately. The product may be purified by extracting unreacted fatty alcohols with hexane.

Sulfation and Sulfonation of Fatty Acids.—The sulfated oils and fats have long been used as wetting and emulsifying agents in the textile industry. The sulfation of ricinoleic acid



$$C_6H_{13}\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH{=}CH(CH_2)_7COOH,$$

which is a constituent of castor oil, may be accomplished in the following manner: 300 parts of ricinoleic acid is mixed with 100 parts of acetic anhydride and sulfated at 0 to 5°C. with 450 parts of concentrated sulfuric acid. The crude sulfuric acid ester is allowed to flow into a cooled and agitated solution of Glauber's salt. The mixture is then settled; the salt solution separated; and the remainder neutralized with a caustic soda solution of 40°Bé. After a few hours, sodium sulfate solution is again separated by decantation or filtration.

The neutralized sulfate is treated with 600 parts of water and then thoroughly stirred with 500 parts of trichloroethylene. The mixture is allowed to settle, and the aqueous solution of the ester separates out as an upper layer, while the trichloroethylene, containing unsulfated oi or fat, forms a lower one. The lower solvent portion is separated, leaving a completely sulfated product behind.[2]

The removal of the unsulfated products constitutes an important problem in such sulfations. Even when an excess of strong sulfuric acid or chlorosulfonic acid is used, some unsulfated material is found in the reaction product along with a mixture of sulfated products, *e.g.*

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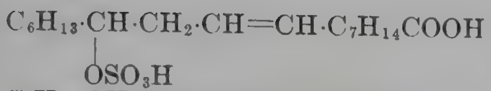
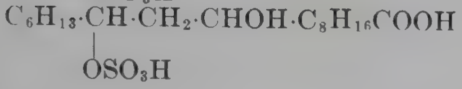
[1] Wolter, U. S. 2,231,979 (1941).

[2] U. S. 1,906,924 (1933).



$$C_6H_{13}{\cdot}\underset{\substack{|\\OSO_3H}}{CH}{\cdot}CH_2{\cdot}CH{=}CH{\cdot}C_7H_{14}COOH$$

(ricinoleylsulfuric acid) and



$$C_6H_{13}{\cdot}\underset{\substack{|\\OSO_3H}}{CH}{\cdot}CH_2{\cdot}CHOH{\cdot}C_8H_{16}COOH$$

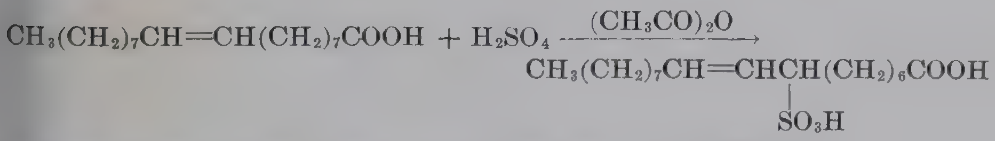
(dihydroxystearylsufuric acid).

Since it is desirable to have a maximum of sulfuric acid in organic combination, it has also been found convenient to decompose the more readily hydrolyzable sulfuric acid esters after sulfonation. Partial saponification of the acid sulfate with the aid of water or dilute acid results in the regeneration of the fatty acids, which can then be separated from the more stable sulfates and sulfonates.

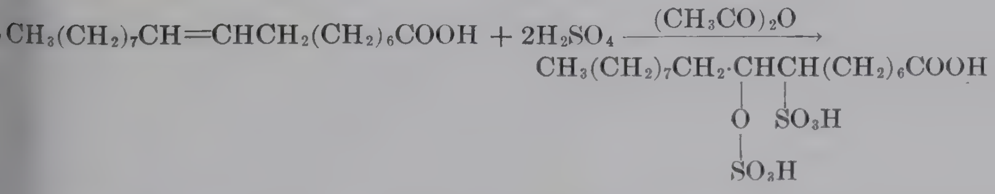
In more recent years, numerous sulfuric acid esters of straight- and branched-chain fatty alcohols have been synthesized, and these are finding wide use as wetting and dispersing agents. It is also possible to obtain true sulfonic acid derivatives that have these valuable characteristics, and the sulfonation of oleic acid will be described to illustrate the procedure.[1]

Oleic acid, 300 parts by weight, is mixed with 100 parts of acetic anhydride, and 300 parts of concentrated sulfuric acid is gradually added to the stirred mass at about 0°C. After the mixture has become soluble in water, the excess of sulfuric acid is washed out with a solution of sodium sulfate. The resultant sulfonic acid, which is clearly soluble in water, may be used as such or in the form of the sodium salt obtained on neutralization.

The following formulas (1) and (2) indicate the probable reactions that occur:



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + H_2SO_4 \xrightarrow{(CH_3CO)_2O} CH_3(CH_2)_7CH{=}CH\underset{\substack{|\\SO_3H}}{CH}(CH_2)_6COOH \qquad (1)$$



$$CH_3(CH_2)_7CH{=}CHCH_2(CH_2)_6COOH + 2H_2SO_4 \xrightarrow{(CH_3CO)_2O} CH_3(CH_2)_7CH_2{\cdot}\underset{\substack{|\\O\\|\\SO_3H}}{CH}\underset{\substack{|\\SO_3H}}{CH}(CH_2)_6COOH \qquad (2)$$

Unlike the turkey red oils obtained by the sulfation of castor oil or ricinoleic acid, these sulfonated products do not readily split off a sulfuric acid radical on boiling with water or with boiling acids or even on treatment with alkalies.

Chlorosulfonic ethyl ester can also be employed for the sulfonation of oleic acid and other unsaturated fatty acids.[2] Thus, 70 parts of oleic acid is stirred at 80°C. with 72 parts of chlorosulfonic ethyl ester, prepared from sulfuryl chloride and alcohol or from ethylene and chlorosulfonic acid. The reaction is continued for 2 hr., and the charge is then diluted with water. About 10 parts of sulfuric acid is added, and the charge is boiled under a reflux condenser until the product dissolves to a clear solution in water. The reaction apparently proceeds according to the following equations:

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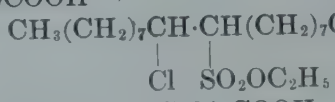
[1] U. S. 1,923,608 (1933).

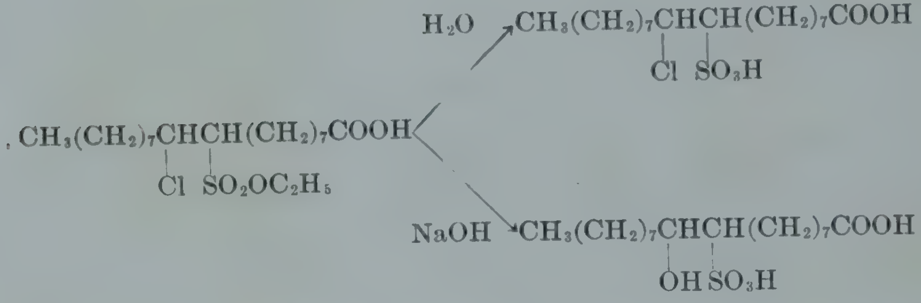
[2] U. S. 1,931,491 (1933).

$$CH_2{=}CH_2 + Cl{\cdot}SO_3H \rightarrow CH_3CH_2OSO_2Cl \quad (1)$$

$$CH_3CH_2OSO_2Cl + CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \rightarrow$$



$$\underset{\displaystyle Cl}{CH_3(CH_2)_7CH}\cdot\underset{\displaystyle SO_2OC_2H_5}{CH}(CH_2)_7COOH \quad (2)$$



$$CH_3(CH_2)_7\underset{\displaystyle Cl}{CH}\underset{\displaystyle SO_2OC_2H_5}{CH}(CH_2)_7COOH \xrightarrow{H_2O} CH_3(CH_2)_7\underset{\displaystyle Cl}{CH}\underset{\displaystyle SO_3H}{CH}(CH_2)_7COOH \quad (3)$$

$$CH_3(CH_2)_7\underset{\displaystyle Cl}{CH}\underset{\displaystyle SO_2OC_2H_5}{CH}(CH_2)_7COOH \xrightarrow{NaOH} CH_3(CH_2)_7\underset{\displaystyle OH}{CH}\underset{\displaystyle SO_3H}{CH}(CH_2)_7COOH \quad (4)$$

Preparation of Sulfoarylalkanes. *With* SO_3 *Dissolved in* SO_2.—The preparation of the sulfoarylalkanes involves three unit processes:

1. Chlorination of a kerosene or dodecane fraction of petroleum to produce "keryl" chloride.
2. Friedel–Crafts condensation of the "keryl" chloride with an aromatic compound—usually benzene.
3. Sulfonation of the aromatic nucleus of the arylalkane. The last two operations may be carried out in one vessel as follows:[1] Dodecyl chloride, 360 parts by weight, is dissolved in a mixture of 200 parts benzene and 1,500 parts of liquid sulfur dioxide, held in a jacketed autoclave provided with a stirring device. Anhydrous aluminum chloride, 200 parts, is added in small portions over a period of about 10 min. The mixture is stirred for 4 hr. To this reaction product is then slowly added, with vigorous agitation, about 500 parts of 20 per cent oleum dissolved in 500 parts of liquid sulfur dioxide. Temperature control is maintained by circulating a cooling fluid through the jacket of the autoclave. The temperature is maintained at not greater than +5°C. for about an hour, the agitation meanwhile continuing. The reaction mixture is now slowly added to ice water. The heat generated by the dilution of the acid mixture is dissipated largely by the evaporation of the liquid sulfur dioxide, which, in turn, prevents the temperature from increasing to an undesirable degree (not higher than 25°C.) while the

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[1] Brandt, U. S. 2,244,512 (1941).

acid is still in a relatively concentrated state. When the mixture is diluted with about twice its volume of water, it is neutralized with caustic soda, digested to break down unstable products, and then washed with gasoline to remove unsulfonated material. The product is finally dried on rolls.

IX. ANALYSIS OF SULFONATIONS AND SULFONATION PRODUCTS

Evaluation of a sulfonation and its products can be determined only by laboratory analysis. Yield of the desired product, as well as isomers and by-products, unreacted material, sulfones, water, tar, and condensation products, are all of importance and must be carefully controlled if success is to be attained. The following methods and procedures are used in sulfonation work and analysis.

1. Progress of Reaction.—This can be done most conveniently by a simple alkali titration, since for every monovalent sulfonic radical produced one molecular weight of sulfuric acid must disappear. In some cases, the color obtained by coupling the product with a diazo compound can be used to follow the progress of the sulfonation. Thus, in the sulfonation of beta-naphthol-7-sulfonic acid to the 3, 7-disulfonic acid, a bluish-colored Bordeaux red with diazonaphthalene shows the monosulfonic acid. A third method, used in naphthalene polysulfonation, is to separate the naphthalene sulfonates and determine their hydrocarbon content by oxidation with vanadic acid in 70 per cent solution. In this way, the proportion of mono- and disulfonic acids can be calculated and hence the extent of the sulfonation. Another method of determining the proportion of mono- and disulfonic acids is to separate their barium salts and then determine the percentage of barium in a sample of the salts quantitatively, from which data it is possible to calculate the percentage of mono- and disulfonates in the mixture. This assumes, of course, that the sulfonation has not proceeded to the trisulfonic acid stage.

2. Determination of Unreacted Hydrocarbons, Sulfones, and Water. For volatile hydrocarbon, it is sufficient to steam-distill the unreacted material out of a sample of the sulfonation mass after dilution with water. In the case of an amine, it is necessary, of course, to make the reaction mixture alkaline before steam-distilling. In cases where the hydrocarbon is not readily volatilized, it is necessary to dilute the sulfonation mixture with water and filter off the unreacted portion. In this case, the result must be corrected for sulfones, which are determined by neutralization of the reaction mass, evaporation to dryness, elimination of the hydrocarbon if it has not volatilized, and extraction of the sulfones in a Soxhlet apparatus with petroleum ether. For water determination in a sulfonation mass, a sample is diluted with a known weight of water and neutralized with excess soda ash, the total water being determined by introducing a stream of carbon dioxide gas and absorbing the water in calcium chloride tubes, finally heating to 180°C. in an oil bath.

Sometimes tars formed in sulfonation processes interfere with separations or analyses. In these cases, it is recommended to hydrolyze the tars with steam and absorb the product with decolorizing carbon.

3. Determination of Isomeric Sulfonic Acids.—Investigation of isomeric acids formed in sulfonation reactions is a complicated procedure in many cases, and special means of separation must often be applied. Derivatives of the isomeric acids are often made; then these are separated, identified, or treated in such a manner that the proportion of the isomers can be determined. A few of these methods are as follows:

a. Dye Method of Selective Reaction.—This method is illustrated in the way G salt, 2-naphthol-6-8-disulfonate, is distinguished from R salt, the 3-6 derivative, in the disulfonation of beta naphthol. Advantage is taken of the different affinity of the two isomerides for certain diazo compounds. For this purpose, diazo-*m*-xylidine solution is prepared, which readily combines with the R salt but not with the G salt, and a sample is titrated to find the amount of R salt.

b. Sulfonchloride Method.—Conversions of isomers into their corresponding sulfonchlorides and separation and identification of these is a common method, particularly in the naphthalene series. The action of phosphorous pentachloride on a dried mixture of the sulfonates readily produces the sulfonchlorides, which are then separated by fractional crystallization from a suitable solvent and identified by melting point data.

c. Bromination Derivative Method.—This method is illustrated in the determination of the relative proportions of metanilic acid and sulfanilic acids in the sulfonation of aniline. Whereas the bromine derivative of metanilic acid is soluble in water, the corresponding derivatives of the ortho and para acids are not soluble. Somewhat different in character is the Vaubel method of analysis, depending on the different reactivity of isomers with bromine. Hydroxy and amino derivatives of benzene and naphthalene are able, under suitable conditions, to absorb one or more atoms of bromine in the ortho and para positions to the hydroxyl or amino group, provided no other substituent interferes. This also applies to the naphthol and naphthylamine sulfonic acids when the sulfonic group does not interfere.

d. Arylamine Salt Method.—The arylamine salts are used as a means of separating and identifying the isomers produced by a sulfonation. These include isomers of naphthalene and β-naphthol sulfonations. The most common amines used are β-naphthylamine, aniline, *p*-toluidine, benzidine, and *m*-xylidine.

e. Chlorine Derivative Method.—This method is applicable to anthraquinone-sulfonic acids. The chlorine derivatives are formed either through the sulfonchlorides by means of thionylchloride or from the sulfonic acids by means of chlorate and hydrochloric acid. The composition of a mixture of isomeric sulfonic acids can be determined from the melting point of the chloranthraquinones after their separation, as in the case of the sulfonchlorides.

f. Salt Solubility Method.—Where possible, advantage is taken of different solubilities of a metal salt for the separation of isomers, as in the case of the calcium and magnesium salts of alpha and beta naphthalenesulfonic acids, potash salts in alpha sulfonation of anthraquinone, and lead salts for separation of naphthalene 2, 6- and 2, 7-disulfonic acids.

CHAPTER VI

AMINATION BY AMMONOLYSIS

By P. H. Groggins and A. J. Stirton

I. GENERAL DISCUSSION

Classification of Reactions

Amination by ammonolysis is the process of forming amines by the action of ammonia. By extension, the use of primary and secondary amines as aminating agents (*aminolysis*) is also included. Such a broadening of the definition permits a comprehensive and integrated presentation of the subject and is fully justified in the light of the similarity of underlying principles and manufacturing practices as well as the industrial utility of the secondary and tertiary amines thus formed.

The ammonolytic reactions may involve simple addition or double decomposition. The latter class includes the replacement of univalent substituents such as —Cl, —OH, $—SO_3H$ and $—NO_2$.

There appear to be six well-defined classes of compounds that are susceptible to conversion to amines. These are

I. Replacement of halogen.

II. Replacement of $—SO_3H$ and of $—OSO_3H$.

III. Ammonolysis of phenols and alcohols.

IV. Conversion of carbonyl compounds.

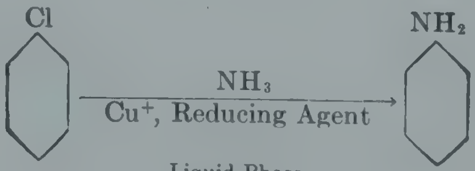
V. Replacement of labile nitro groups.

VI. Addition reactions, such as the addition of NH_3 to carbon dioxide, alkylene oxides, acrylonitrile, and cyanamide.

The following equations illustrate the classes of compounds previously mentioned and indicate the types of syntheses made possible by this unit process.

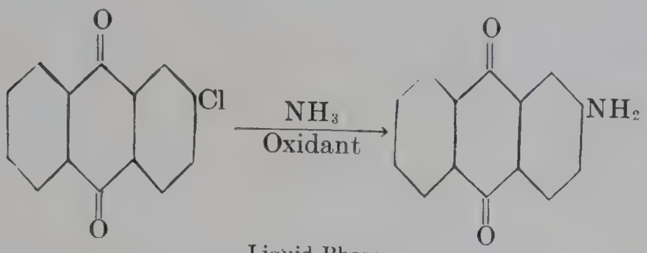
Class I. Replacement of Halogen.

1. Aniline from chlorobenzene.



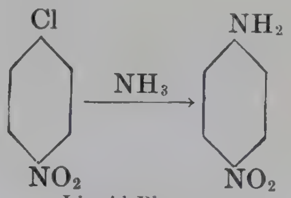
Liquid Phase
Vapor Phase

2. 2-Aminoanthraquinone from 2-chloroanthraquinone.



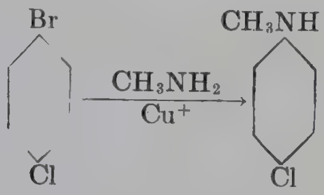
Liquid Phase

3. *p*-Nitroaniline from *p*-nitrochlorobenzene.

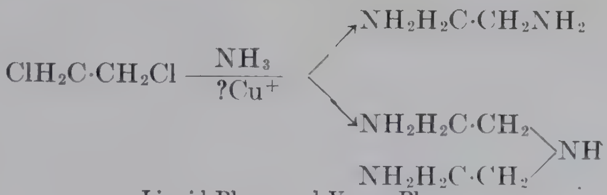


Liquid Phase

4. 4-Chloro-(N-methyl-)aniline from 4-chlorobromobenzene.



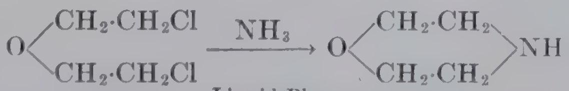
5. Ethylenediamine and diethylenetriamine from ethylene dichloride.



$$ClH_2C\cdot CH_2Cl \xrightarrow[?Cu^+]{NH_3} \left\{\begin{array}{l} NH_2H_2C\cdot CH_2NH_2 \\ \\ \left.\begin{array}{l} NH_2H_2C\cdot CH_2 \\ NH_2H_2C\cdot CH_2 \end{array}\right> NH \end{array}\right.$$

Liquid Phase and Vapor Phase

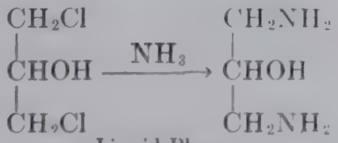
6. Morpholine from *sym*-dichloroethyl ether.



$$O\left<\begin{array}{l} CH_2\cdot CH_2Cl \\ CH_2\cdot CH_2Cl \end{array}\right. \xrightarrow{NH_3} O\left<\begin{array}{l} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{array}\right>NH$$

Liquid Phase

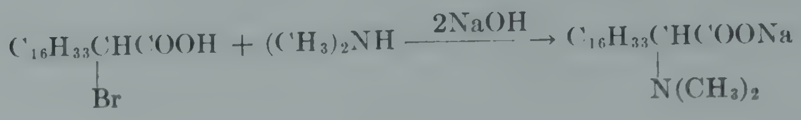
7. 1, 3-Diaminopropanol from 1, 3-dichloropropanol-2.



$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} \xrightarrow{NH_3} \begin{array}{l} CH_2NH_2 \\ | \\ CHOH \\ | \\ CH_2NH_2 \end{array}$$

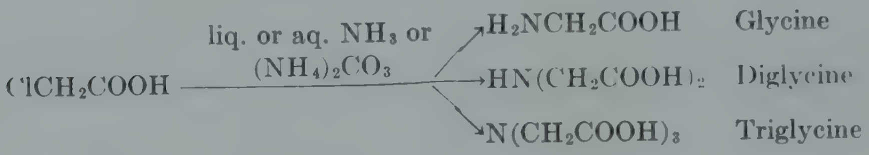
Liquid Phase

8. Alpha dimethylaminostearic acid from *a*-bromostearic acid.



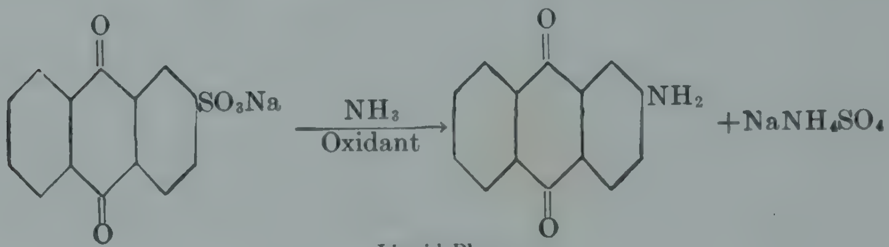
$$C_{16}H_{33}\underset{\substack{|\\ Br}}{C}HCOOH + (CH_3)_2NH \xrightarrow{2NaOH} C_{16}H_{33}\underset{\substack{|\\ N(CH_3)_2}}{C}HCOONa$$

9. Glycines from chloroacetic acid.


$ClCH_2COOH$
liq. or aq. NH_3 or
$(NH_4)_2CO_3$
H_2NCH_2COOH Glycine
$HN(CH_2COOH)_2$ Diglycine
$N(CH_2COOH)_3$ Triglycine

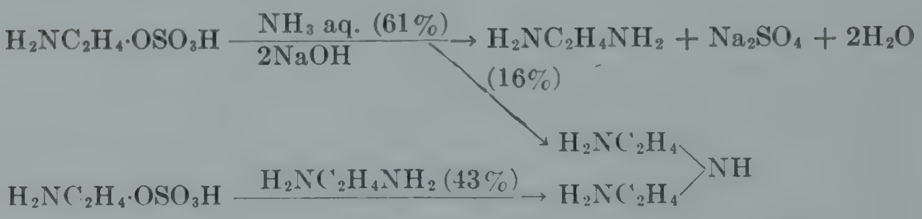
Class II. Replacement of —SO_3H and of —OSO_3H Groups.

1. 2-Aminoanthraquinone from sodium anthraquinonesulfonate.


O
O
SO_3Na
NH_3
Oxidant
O
O
NH_2
$+NaNH_4SO_4$

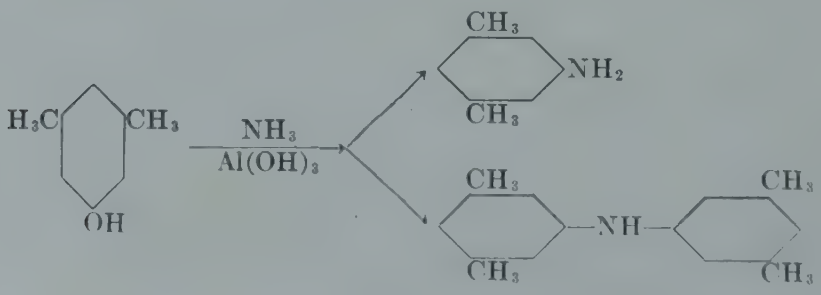
Liquid Phase

2. Ethylenediamine and diethylenetriamine from aminoethyl hydrogen sulfate.

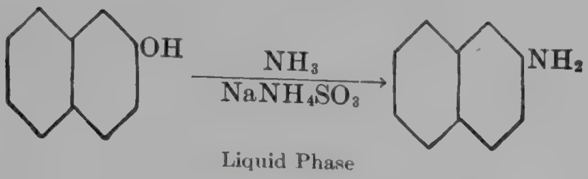

$H_2NC_2H_4{\cdot}OSO_3H$
NH_3 aq. (61%)
2NaOH
$H_2NC_2H_4NH_2 + Na_2SO_4 + 2H_2O$
(16%)
$H_2NC_2H_4$
NH
$H_2NC_2H_4$
$H_2NC_2H_4{\cdot}OSO_3H$
$H_2NC_2H_4NH_2$ (43%)

Class III. Ammonolysis of Phenols and Alcohols. *Group A. Phenols and Naphthols.*

1. *sym*-Xylylamines from *sym*-xylenol.


H_3C
CH_3
OH
NH_3
$Al(OH)_3$
CH_3
NH_2
CH_3
CH_3
—NH—
CH_3
CH_3
CH_3

2. β-Naphthylamine from β-naphthol.



Group B. Alcohols.

1. Methylamines from methanol.

$$CH_3OH \xrightarrow[AlPO_4]{NH_3} \left. \begin{array}{l} CH_3NH_2 \\ (CH_3)_2NH \\ (CH_3)_3N \end{array} \right.$$

Vapor Phase

2. Butylamines from butanol.

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH \xrightarrow[Al_2O_3]{NH_3} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

Vapor Phase

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH \xrightarrow[\text{Ni Catalyst}]{NH_3 + H_2} \left. \begin{array}{l} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2NH_2 \\ (CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)_2NH \\ (CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)_3N \end{array} \right.$$

Vapor Phase

3. N-Methyloctadecylamine from octadecyl alcohol.

$$CH_3(CH_2)_{16}CH_2OH \xrightarrow[\text{Alumina Gel}]{CH_3NH_2} CH_3(CH_2)_{16}CH_2NHCH_3$$

Liquid Phase

Group C. Hydroxy and Alkoxy Propionitriles.

1. β-Alanine from ethylene cyanhydrin.

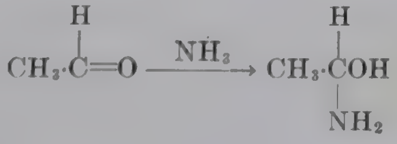
$$HOCH_2CH_2CN \xrightarrow{NH_3\ aq.} H_2NCH_2CH_2COOH$$

2. β-Alanine from methoxypropionitrile.

$$CH_3OCH_2CH_2CN \xrightarrow{NH_3\ aq.} H_2NCH_2CH_2COOH$$

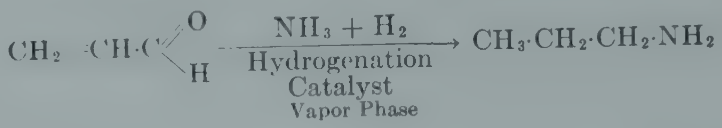
Class IV. Conversion of Carbonyl Compounds. *Conversion of Aldehydes.*

1. Acetaldehydeammonia by addition.

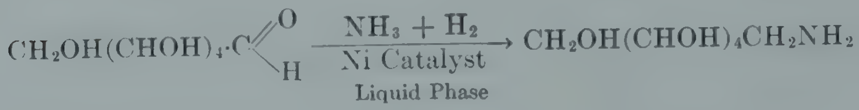


$$CH_3{\cdot}\overset{H}{\overset{|}{C}}{=}O \xrightarrow{NH_3} CH_3{\cdot}\underset{NH_2}{\underset{|}{\overset{H}{\overset{|}{C}}}}OH$$

2. *n*-Propylamine from acrolein.

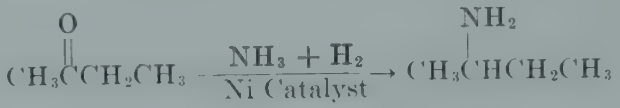

CH₂ :CH·C O H
NH₃ + H₂
Hydrogenation Catalyst
Vapor Phase
CH₃·CH₂·CH₂·NH₂

3. Glucosamine from glucose.


CH₂OH(CHOH)₄·C O H
NH₃ + H₂
Ni Catalyst
Liquid Phase
CH₂OH(CHOH)₄CH₂NH₂

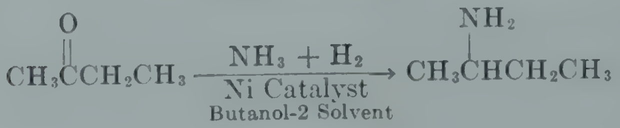
Conversion of Ketones.

1*a*. 2-Aminobutane from methyl ethyl ketone.



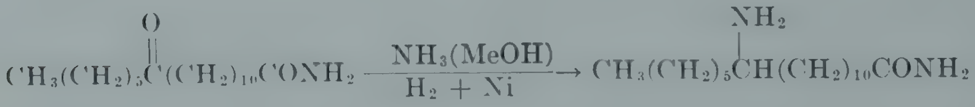
$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \xrightarrow[\text{Ni Catalyst}]{NH_3 + H_2} CH_3\overset{\overset{NH_2}{|}}{C}HCH_2CH_3$$

1*b*.



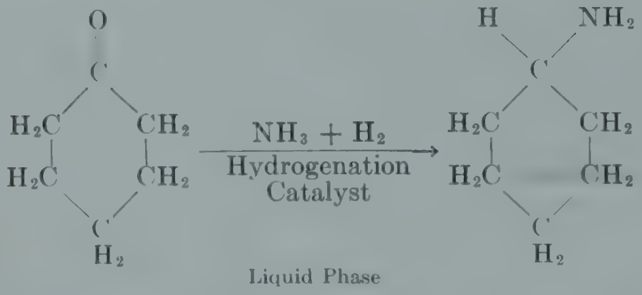
$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \xrightarrow[\substack{\text{Ni Catalyst}\\ \text{Butanol-2 Solvent}}]{NH_3 + H_2} CH_3\overset{\overset{NH_2}{|}}{C}HCH_2CH_3$$

2. 12-Aminostearamide from 12-ketostearamide.

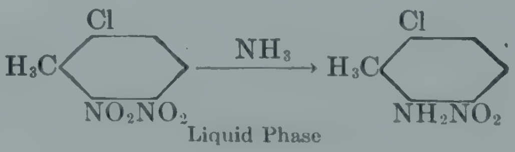


$$CH_3(CH_2)_5\overset{\overset{O}{\|}}{C}(CH_2)_{10}CONH_2 \xrightarrow[H_2 + Ni]{NH_3(MeOH)} CH_3(CH_2)_5\overset{\overset{NH_2}{|}}{C}H(CH_2)_{10}CONH_2$$

3. Cyclohexylamine from cyclohexanone.

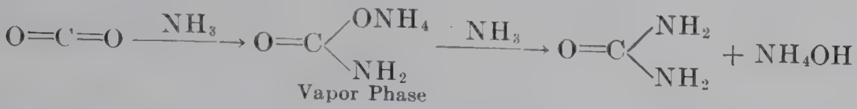

O
C
H₂C
CH₂
H₂C
CH₂
C
H₂
NH₃ + H₂
Hydrogenation Catalyst
Liquid Phase
H
NH₂
C
H₂C
CH₂
H₂C
CH₂
C
H₂

Class V. Replacement of Labile Nitro Groups. 6-Chloro-3-nitro-*o*-toluidine from 5, 6-dinitro-*o*-chlorotoluene.


Cl
H₃C
NO₂NO₂
NH₃
Liquid Phase
Cl
H₃C
NH₂NO₂

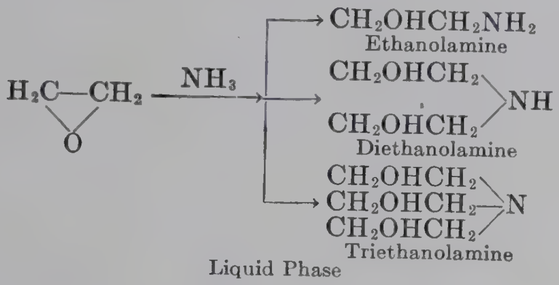
Class VI. Addition Reactions.

1. Urea from carbon dioxide.

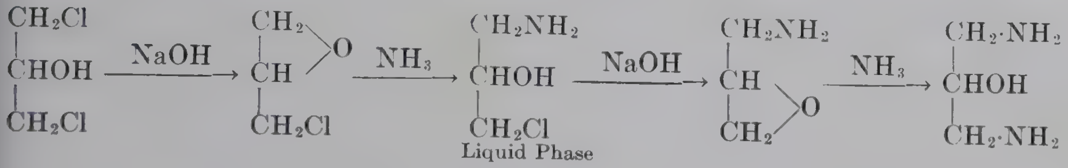


$$O{=}C{=}O \xrightarrow{NH_3} \underset{\text{Vapor Phase}}{O{=}C\begin{smallmatrix} ONH_4 \\ NH_2 \end{smallmatrix}} \xrightarrow{NH_3} O{=}C\begin{smallmatrix} NH_2 \\ NH_2 \end{smallmatrix} + NH_4OH$$

2a. *Alkanolamines from Alkylene Oxides.* 1. Ethanolamines from ethylene oxide.


H₂C—CH₂
O
NH₃
CH₂OHCH₂NH₂
Ethanolamine
CH₂OHCH₂
CH₂OHCH₂
NH
Diethanolamine
CH₂OHCH₂
CH₂OHCH₂
CH₂OHCH₂
N
Triethanolamine
Liquid Phase

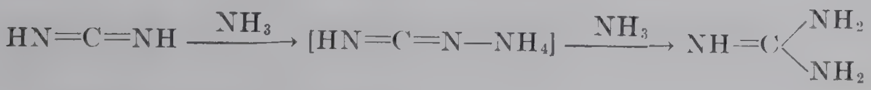
2b. 1, 3-Diaminopropanol from epichlorohydrin.


CH₂Cl
CHOH
CH₂Cl
NaOH
CH₂
CH
CH₂Cl
O
NH₃
CH₂NH₂
CHOH
CH₂Cl
Liquid Phase
NaOH
CH₂NH₂
CH
CH₂
O
NH₃
CH₂·NH₂
CHOH
CH₂·NH₂

3. β-Alanine from acrylonitrile.

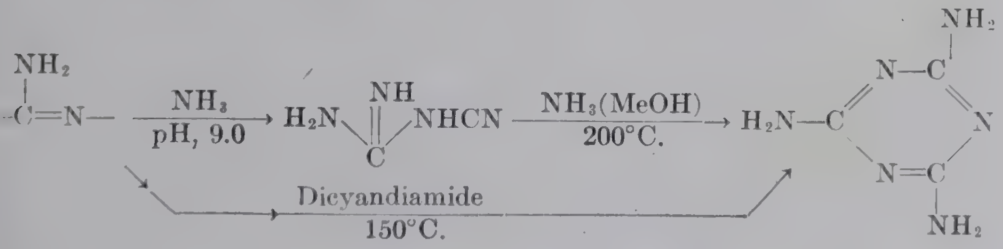
$$CH_2{=}CHCN \xrightarrow{NH_3} \underset{\beta\text{-Aminopropionitrile}}{H_2NCH_2CH_2CN} \xrightarrow{H_2O} H_2NCH_2CH_2COOH$$

4. Guanidine from cyanamide.



$$HN{=}C{=}NH \xrightarrow{NH_3} [HN{=}C{=}N{-}NH_4] \xrightarrow{NH_3} NH{=}C\begin{smallmatrix} NH_2 \\ NH_2 \end{smallmatrix}$$

5. Melamine from cyanamide.


NH₂
—C=N—
NH₃
pH, 9.0
H₂N
NH
C
NHCN
NH₃(MeOH)
200°C.
H₂N—C
N—C
NH₂
N
N=C
NH₂
Dicyandiamide
150°C.

II. THE AMINATING AGENT

The aminating agent may be NH_3 employed as liquid ammonia, as a solution in water or an organic solvent, or as a gas in a vapor-phase reaction or evolved from solid compounds such as urea or ammonium salts. In each case, it is reasonable to consider that ammonolysis is actually brought about by NH_3. In selection of the particular aminating agent, consideration would be given to the temperature and pressure conditions normally required for a given type of compound, the type of catalyst that might be effective, the stability and solubility of the compound to be aminated, and the avoidance of side reactions such as hydrolysis or the formation of secondary amines. Some of the properties of the aminating agents are now briefly reviewed.

Liquid Ammonia.—The properties of liquid ammonia are compared with those of water in Table I.

Table I.—Properties of Ammonia and Water

Properties	Liquid ammonia	Water
Melting point	−77.7°C.	0°C.
Boiling point	−33.35°C.	100°C.
Specific heat, cal./gm. at b.p.	1.07	1.01
Specific gravity at 20°C	0.607	0.9982
Critical temperature	131°C.	365°C.
Critical pressure, atmos	112	195
Surface tension, dynes/cm	23.4 at 11°C.	72.8 at 20°C.
Dielectric constant	22.7 at −50°C.	81.1 at 18°C.
Mobility of K ion, cm./sec./volt	0.0176 at −33°C.	0.0067 at 20°C.
Specific conductivity, mhos	1.3×10^{-7} at −79°C.	4×10^{-8} at 18°C.
Ion product constant	1.9×10^{-33} at 50°C.	0.72×10^{-14} at 18°C.

Liquid ammonia resembles water in its general physical and chemical properties as is apparent in the values of Table I. It can also be seen, from the boiling point, for example, that the technic of ammonolysis may be different, depending on whether liquid ammonia or aqueous ammonia is used as the aminating agent.

Both ammonia and water are associated liquids. They form compounds with salts, are good solvents, and, although virtual nonconductors themselves, effect the ionization of electrolytes. The ionizing power of liquid ammonia is largely due to the high speed at which the ions of dissolved electrolytes move in this solvent.

Added electrolytes may increase the rate of ammonolysis. Ammonium salts have been found to be quite effective, and the explanation has been that "acid catalysis" occurs, since $N\overset{+}{H}_4$ is an acid in the ammonia system just as is $H_3\overset{+}{O}$ in the aqueous system. Neutral electrolytes, however, such as $NaNO_3$, may also influence the rate of ammonolysis; and although this behaviour is not fully understood, catalysis by ammonium salts may now be regarded as a special case of a more general effect for which the term "electrolyte catalysis" has been suggested.[1]

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[1] Audrieth, Scott, and Hill, *J. Am. Chem. Soc.*, **64,** 2498–2499 (1942).

The data of Table II on the ammonolysis of chloroacetic acid in liquid ammonia[1] show that ammonium carbamate is a superior catalyst; there are some differences in the other ammonium salts; but they are all good catalysts, whereas NaC1 and $NaNO_3$ are not.

TABLE II.—EFFECT OF ADDED ELECTROLYTES IN AMMONOLYSIS OF CHLOROACETIC ACID
In Liquid Ammonia in Sealed Tubes at 25°C.
Mole Ratio $ClCH_2COOH:NH_3$:Added Electrolyte = 1:20:2

Added electrolyte	Time, hr.	Conversion, %, to primary amino acid
None	78	41.5
NaCl*	53	42.6
$NaNO_3$*	53	42.9
$NH_2CO_2NH_4$*	34	51.8
$CH_3CO_2NH_4$	81	53.1
NH_4NO_3	67	53.5
NH_4Cl	61	59.6

* Not completely soluble.

The effect of ammonium salts in the ammonolysis of chloroacetic acid in liquid ammonia may be explained by the following three equations.

1. $ClCH_2COOH + NH_3 \rightarrow ClCH_2CO\bar{O} + \overset{+}{N}H_4$
2. $ClCH_2CO\bar{O} + 2NH_3 \rightarrow NH_2CH_2CO\bar{O} + \overset{+}{N}H_4 + \bar{C}l$
3. $\overset{+}{N}H_4 + NH_2CH_2CO\bar{O} \rightleftarrows \overset{+}{N}H_3CH_2CO\bar{O} + NH_3$

Liquid ammonia is a more basic solvent than water, has a greater affinity for protons, and favors the existence of $NH_2CH_2CO\bar{O}$ rather than the zwitter ion $\overset{+}{N}H_3CH_2CO\bar{O}$. The ion $NH_2CH_2CO\bar{O}$ has a free pair of electrons on the nitrogen atom and is open to further reaction with the halogen compound, leading to secondary and tertiary ammonolytic products. Thus liquid ammonia favors the formation of secondary and tertiary amines more than does aqueous ammonia. Large concentrations of $\overset{+}{N}H_4$, such as those obtained by the deliberate addition of ammonium salts, cause the equilibrium in Eq. (3) to go to the right, decreasing the concentration of the ion $NH_2CH_2CO\bar{O}$ and decreasing the amount of the secondary and tertiary products of ammonolysis.

The four ammonium salts of Table III differ in their effectiveness. The exceptional catalytic behaviour of $NH_2CO_2NH_4$ cannot be accounted for easily. Another anomaly is the behaviour of NH_4NO_3, which increases the rate of ammonolysis of chloroacetic and of α-chloropropionic acid but decreases the rate of reaction of α-bromoisovaleric acid.

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[1] SISLER, and CHERONIS, *J. Org. Chem.*, **6**, 467–478 (1941).

The ammonolysis of 9-phenyl-9-chlorofluorene in liquid ammonia (Table III) is an example of a case in which neutral electrolytes as well as ammonium salts are effective catalysts.[1]

TABLE III.—EFFECT OF ADDED ELECTROLYTES IN AMMONOLYSIS OF 9-PHENYL-9-CHLOROFLUORENE

In Liquid Ammonia, 3 Hr. at 25.08°C.; Original Concentration of $C_{19}H_{13}Cl = 0.075$ Moles/Liter; 0.1 Mole/Liter of Added Electrolyte.

Added electrolyte	None	NH_4NO_3	$NaNO_3$	NH_4Cl	NaCl
Concentration of unreacted $C_{19}H_{13}Cl$, moles/liter	0.054	0.034	0.042	0.043	0.046

In no case is the energy of activation lower than that for the uncatalyzed reaction. The ordinary concept that catalysis involves a lower energy of activation is not necessarily applicable to catalysis of ammonolytic reactions in liquid ammonia.

Liquid ammonia may be introduced into reaction systems, and ammonolysis then carried out at temperatures higher than the critical temperature. These are really examples of the use of gaseous ammonia as the aminating agent or of ammonia dissolved in one of the reactants or in an inert organic solvent.

Aqueous Ammonia.—It is quite probable that aqueous ammonia will continue to be the aminating agent used in the greatest amount and in the greatest number of cases. It has the advantage of greater convenience in handling and general applicability, and it readily dissolves sulfonic acids, for example, as well as catalysts such as copper salts or $KClO_3$. Disadvantages may be the limited solubility of chloro compounds and the occurrence of hydrolysis along with ammonolysis.

TABLE IV.—SOLUBILITY OF AMMONIA IN WATER AT 760 MM.

Temperature, °C.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Gm. NH_3/100 gm. of solution, %	47.4	40.7	34.1	29.0	25.3	22.1	19.3	16.2	13.3	10.2

Aqueous ammonia might be employed under a variety of conditions, since the solubility of ammonia in water is influenced by both temperature and pressure. In practice, however, ammonolysis with aqueous ammonia usually refers to the use of 25 to 28 per cent aqueous ammonia under pressure at temperatures greater than 100°C. Table IV illustrates the solubility of NH_3 in water as a function of temperature at 1 atmos. pressure.

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[1] WILLIAMSON, ANDERSON, and WATT, *J. Am. Chem. Soc.*, **65**, 49–51 (1943); **66**, 376–379 (1944).

Ammonolysis with aqueous ammonia should be interpreted as being brought about by NH_3, not by NH_4OH. As water is only a very weak acid, the ammonia addition product is very unstable, and ammonium hydroxide exists in aqueous ammonia as a weak base present in small amount. To account for the weakness of ammonium hydroxide, it has been assumed that a hydrogen atom acts as a bond:

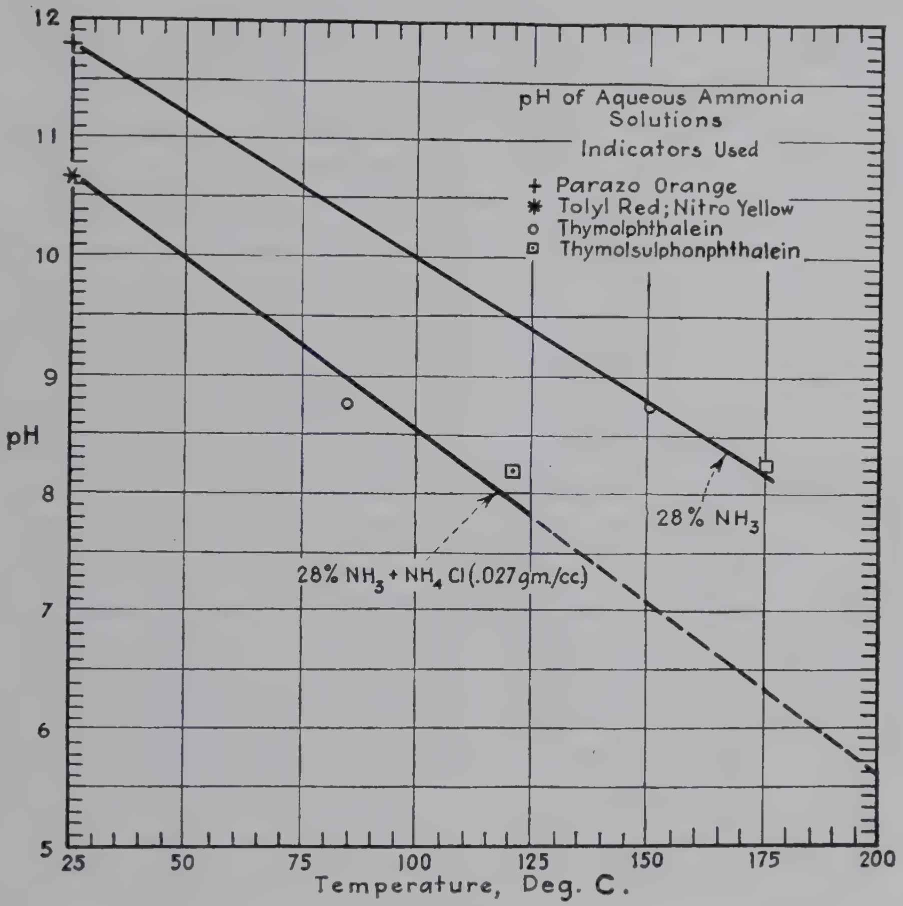

FIG. 1.—pH of aqueous ammonia.

$$NH_3 + H_2O \rightleftarrows H:\overset{H}{\underset{H}{\overset{..}{\underset{..}{N}}}}:H:\overset{..}{\underset{..}{O}}:H \rightleftarrows N\overset{+}{H}_4 + O\overset{-}{H}$$

The presence of hydroxyl ions from the dissociation of ammonium hydroxide, alkyl or arylammonium hydroxide, or water is responsible for the simultaneous formation of hydroxy compounds. Thus, in the amination of chlorobenzene and chloroanthraquinones by this unit process, phenol and hydroxyanthraquinones, respectively, are found accompanying the amino compounds in the reaction product:

$$C_6H_5Cl \xrightarrow{aq.\ NH_3} C_6H_5NH_2 + \text{Some } C_6H_5OH + NH_4Cl$$

In the preparation of aniline, the concomitant formation of phenol is not always objectionable; the situation is entirely different in the preparation of compounds such as 2-aminoanthraquinone and other solid amines which cannot be purified by inexpensive physical or chemical means.

Secondary and tertiary amines are almost always formed during the ammonolysis of halogeno and hydroxy compounds, the quantity depending on the specific reactants, the NH_3 ratio, and other conditions employed. By the reintroduction of these products in subsequent charges, their further formation is stated to be inhibited.[1]

Usually much higher temperatures and the use of different catalysts are required for the ammonolysis of aromatic than for aliphatic halogeno compounds. It is therefore not easy to generalize on the conditions that may lead to secondary or tertiary amine by-products in the ammonolysis of all types of halogeno compounds.

Colorimetric studies in sealed glass tubes indicate that ammonia combines with water, above the critical temperature of NH_3, to form ammonium hydroxide.[2] The curves of Fig. 1 show that the pH of 28 per cent aqueous ammonia decreases, however, with rising temperature, from 11.8 at room temperature to only 8.2 at 175°C., under approximately 500 lb. per sq. in. pressure. The pH drops off more rapidly when hydrogen chloride or its ammonium salt is introduced, corresponding to conditions prevailing during ammonolysis. At 175°C., the pH of neutrality is 5.7.

Properties of Aqueous Ammonia. Vapor Pressures.—Wilson has investigated the partial pressures of aqueous ammonia over a wide range of both concentration and temperature.[3] Some of his data are presented in Figs. 2 and 3. The curves (Fig. 2) show that the partial pressures of the water vapor in the vapor phase are not strictly proportional to the water content of the solution phase. There is a slight, consistent negative deviation from the ideal value entirely in harmony with the idea that, below the critical temperature of NH_3, solutions of ammonia are not completely physical mixtures of two components.

Perman also observed a similar deviation with respect to Henry's law; but on account of the slightness of the deviation, he concluded that an aqueous solution of ammonia behaves as a mixture of two liquids the

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[1] Williams, U. S. 1,775,360 (1930); Hale, U. S. 1,932,518 (1933); Swallen, U. S. 1,926,691 (1933); Herold and Smeykal, U. S. 2,068,132 (1937); Arnold, U. S. 1,799,-722; Reissue 19,632(1935).

[2] Groggins and Stirton, *Ind. Eng. Chem.*, **25**, 42 (1933).

[3] Wilson, *Univ. Illinois Eng. Expt. Sta. Bull.* 146 (1925).

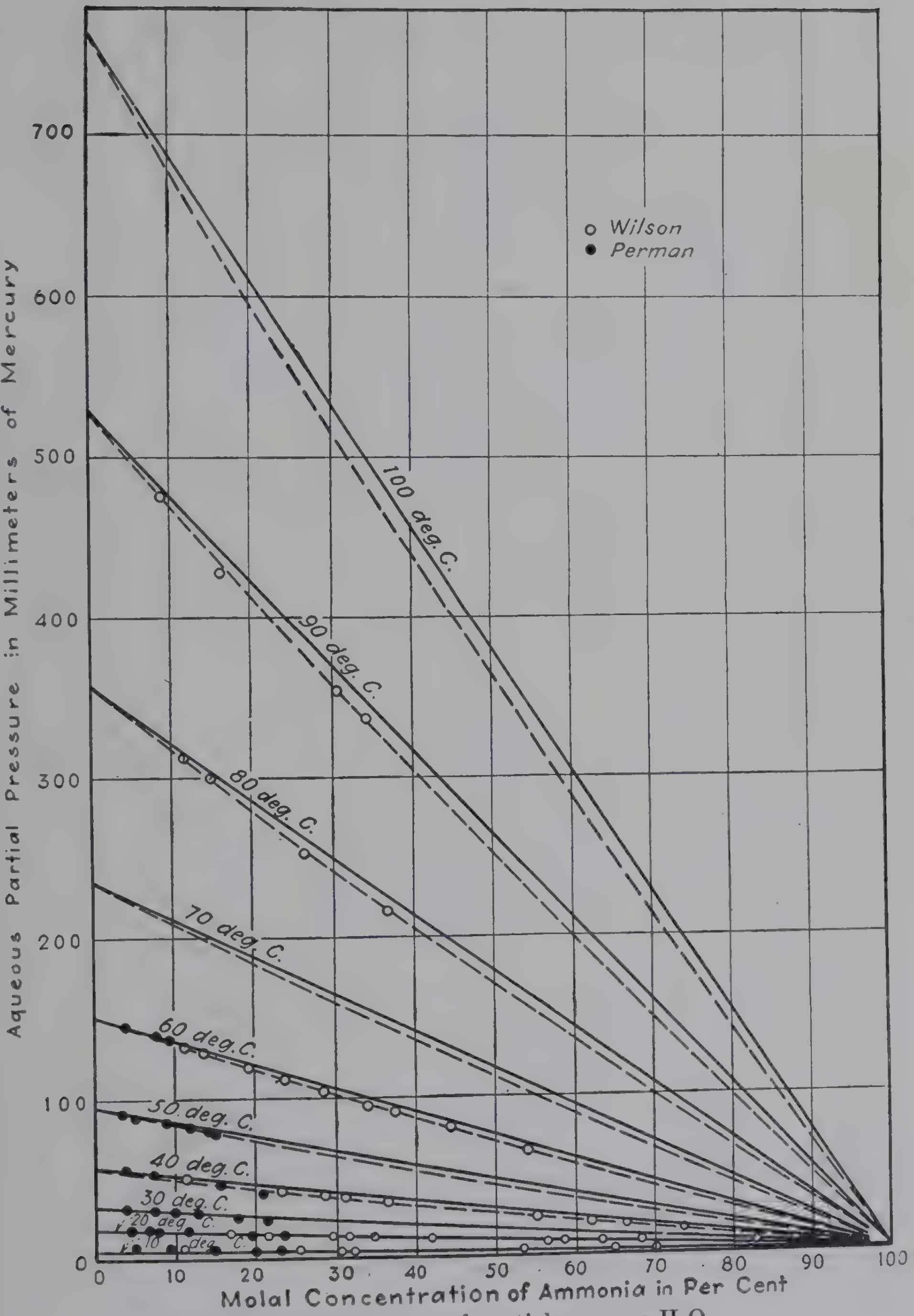

Fig. 2.—Raoult's law and partial pressure H_2O.

boiling points of which are far removed from each other.[1] The lowering of the vapor pressure of water by the ammonia follows Raoult's law closely, showing that the molecular weight of NH_3 in solution is normal and no large quantity of hydrate is formed.

Surface Tension.—King, Hall, and Ware, in studying the properties of the ammonia-water system, concluded that "It is evident from the surface tension and thermodynamic standpoint that the system does not deviate radically from what is to be expected of a *perfect mixture*."[1]

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[1] Perman, *J. Chem. Soc.*, **79**, 718 (1901); **83**, 1168 (1903).

It appears, therefore, that ammonolysis with aqueous ammonia is similar to ammonolysis with ammonia gas dissolved in any comparatively inert solvent. Indeed, the pH studies and the review of the properties and reactions of aqueous ammonia practically compel the adoption of this viewpoint.

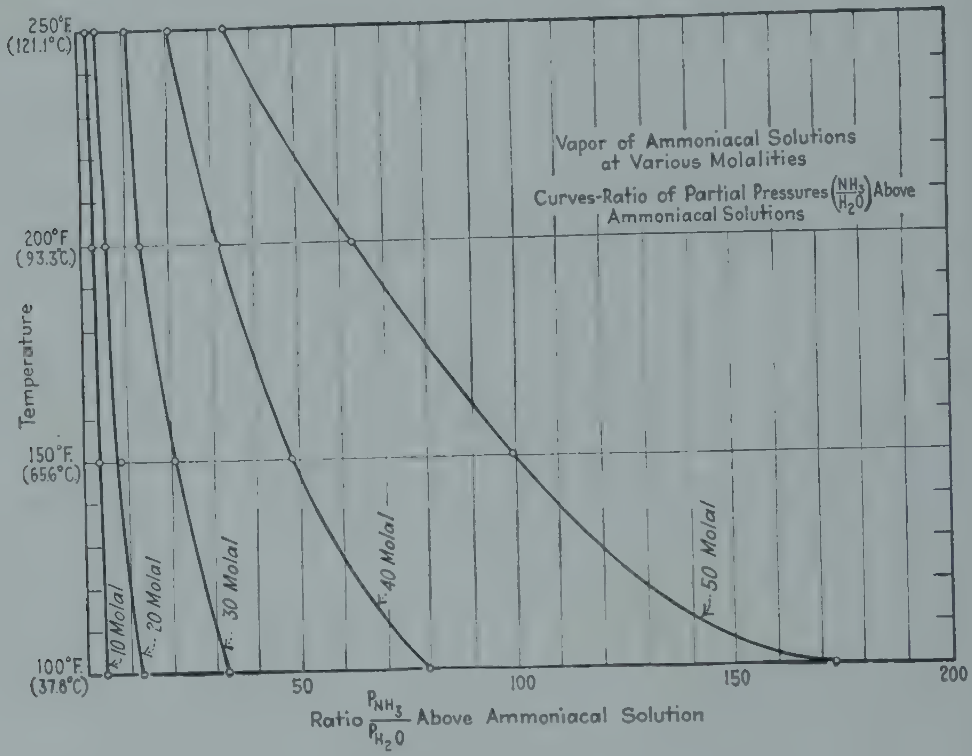

Fig. 3.—Ratio $\frac{P_{NH_3}}{P_{H_2O}}$.

Comparative NH_3 *and* H_2O *Vapor Pressures.*—The effects of operating with aqueous NH_3 solutions of various concentrations may be appreciated by a study of the curves of Fig. 3, which relate to the proportionality P_{NH_3}/P_{H_2O}.

From these data, it can be observed that with increasing NH_3 concentration, there is a comparative acceleration in the quotient P_{NH_3}/P_{H_2O}.[2] For a definite concentration, however, the partial pressure of ammonia does not increase so rapidly as the water-vapor pressure when the temperature of the solution is increased. From this, it may be predicted that there is a proportionally increased activity of water vapor at increasing temperatures. Thus, in order to obtain the best results during ammonolysis, it is advisable to employ the lowest possible temperature that produces the necessary energy-intensity factor. This condition is, in a measure, realized by increasing the molal concentration of NH_3 in the ammonia employed.

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[1] King, Hall, and Ware, *J. Am. Chem. Soc.*, **52**, 5128 (1930).

[2] Wilson, *op. cit.*

Ammonia Dissolved in an Inert Solvent.—Organic compounds are soluble in liquid ammonia to some extent, and, conversely, gaseous NH_3 is soluble in some organic liquids.

The use of an inert organic solvent to dissolve gaseous ammonia and also the compound to be aminated would seem to be a very attractive procedure since the reactants are in intimate contact and a side reaction such as hydrolysis would not be possible. Actually, however, there are some difficulties with the use of NH_3 in an organic solvent. The solvent, *e.g.*, an alcohol, may not be entirely inert. A low ratio of the solvent must adequately dissolve both the ammonia and the compound to be aminated, and the solvent must be easily recovered.

The solubility of NH_3 in organic solvents is less than it is in water. Compared with the data of Table IV, the solubility of NH_3 in CH_3OH at 0, 10, 20 and 30° is as follows, respectively: 29.3, 24.2, 19.2, and 14 per cent. The solubility of NH_3 in hydrocarbons and halogeno compounds is usually less than 1 per cent at room temperature.

Liquid ammonia is a better solvent for organic compounds than organic compounds are for gaseous ammonia. The lower aliphatic alcohols, benzyl and cinnamyl alcohol, ethylene glycol and glycerol, are miscible with liquid ammonia, and phenol and the polyhydroxybenzenes dissolve readily. Benzene dissolves readily at 20°; the lower chloroalkanes are readily soluble; and chlorobenzene is slightly soluble. Data are lacking on the solubility of NH_3 in organic solvents under the various temperature and pressure conditions that might be used in ammonolysis.

III. SURVEY OF AMINATION REACTIONS

Class I. Conversion of Halogeno Compounds

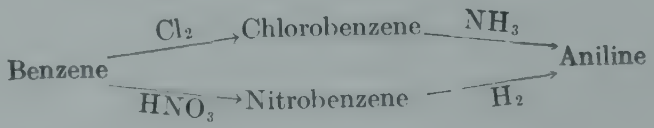
The halogen of alkyl halides is generally readily susceptible to replacement by the $—NH_2$ group, but aromatically bound halogen usually requires more drastic treatment. Because of economic considerations, the chlorine derivatives are ordinarily employed, but bromine-substituted compounds are sometimes used because they usually lead to the formation of primary amines of higher purity under milder operating conditions.

When a catalyst is essential, copper, its oxides, and salts are preferred, and these are almost always used in the ammonolysis of compounds wherein the halogen is attached to an aromatic nucleus not containing negative substituents, *e.g.*, chlorobenzene, chloroxenene, and chloronaphthalene. In the treatment of alkylene, nitrophenyl, and anthraquinone halides, copper catalysts are not essential but may be used to accelerate the reaction.

The following brief survey is merely a presentation of typical syntheses. The factors governing these reactions, as well as an insight into the details of technical operations in the manufacture of some of the more important amino compounds, will be discussed later in this chapter.

Aniline from Chlorobenzene.[1]—The process consists in treating chlorobenzene with aqueous ammonia in the presence of cuprous oxide. Amination proceeds slowly under 160°C. and very rapidly at 210°C. At still higher temperatures, there is a distinct tendency to phenol formation and decomposition. A temperature range of 200 to 210°C. gives satisfactory results. At this temperature, with a 6:1 ammonia ratio of 28 per cent aqueous ammonia, the pressure on the system will be about 850 to 950 lb. per sq. in. At the conclusion of the reaction, the vapors leaving the pressure system are expanded and cooled below 100°C. in a suitable pipe condenser or dephlegmating column. Most of the ammonia continues to an absorption system in which the gas is recovered and concentrated for reuse.

Although only 2 moles of NH_3 is required theoretically per mole of chlorobenzene treated, experience has shown that better results are obtained with higher ratios. In plant practice, a ratio of only 4 to 6 moles is employed, for it is necessary to excercise the strictest economy in the preparation of such a low-priced intermediate. In the two competitive methods of producing aniline,



the cost of introducing the nitrogen-containing group is the most important item of expense. Since the price of nitric acid is now generally dependent on the cost of synthetic ammonia, neither process has any pronounced advantage in material or processing costs.

Aniline can also be prepared by the vapor-phase ammonolysis of chlorobenzene.[2] A catalyst prepared from a copper salt and the ammonium salt of vanadic, tungstic, or phosphoric acid has been found to be somewhat effective. The vapors of chlorobenzene and ammonia are passed over such a catalyst maintained at 400°C., and a per-pass conversion to aniline of 10 per cent is obtained.

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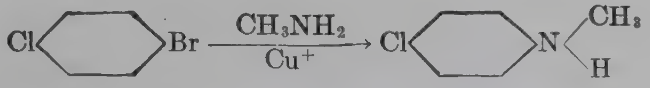
[1] Patents assigned to the Dow Chemical Co.: U. S. 1,607,824 (1926); 1,726,170; 1,726,171; 1,726,172; 1,726,173; 1,729,775 (1929); 1,775,360 (1930); 1,823,025; 1,823,026 (1931); 1,840,760; 1,885,625 (1932); 1,932,518 (1933); 2,106,962 (1935).

[2] Mathes and Prahl, U. S. 2,001,281 (1935).

Preparation of Chloroanilines.—The comparative ease in replacing the bromine atom of 4-chlorobromobenzene can be taken advantage of in the preparation of 4-chloroaniline as well as 4-chloro-(N-methyl-)aniline.[1]



For the preparation of the substituted amine, 4-chlorobromobenzene is treated with aqueous monomethylamine (33 per cent) in the presence of cuprous chloride at 110°C.

The direct replacement of both chlorine atoms from *p*- or *o*-dichlorobenzene is very difficult, and a satisfactory process has not as yet been developed. A high ammonia ratio and 40 to 50 per cent ammonia is desirable. The presence of cuprous copper in quantities sufficient to form an organo copper complex is helpful. The difficulty in effecting the ammonolysis of dichlorobenzenes is attributed to the establishment of an equilibrium after the formation of a monoamine and to the change in the pH of the aminating solution due to the concentration of HCl or NH_4Cl.

Preparation of Aliphatic Amines.—In the amination of aliphatic halides, it is comparatively easy to replace the halogen by the amino group. The alkyl chlorides are readily converted to the corresponding amines by treatment with aqueous ammonia under pressure. The separation of the primary, secondary, and tertiary amines thus formed is made by taking advantage of slight differences in their physical constants or chemical reactivity.

In the aromatic series, the replacement of two chlorine atoms in the phenyl or anthraquinone nucleus is generally very difficult, even when a nitro group is present. In contrast, however, ethylenediamine can readily be obtained from the corresponding dichloro compound.

Ethylenediamines.—Ethylenediamine and the polyamines can readily be prepared by treating the dichloride with aqueous ammonia under pressure at 100 to 180°C. To secure a preponderance of primary amine, it is necessary to employ concentrated ammonia in large excess. The process may be carried out in a continuous manner (see page 391) and can also be adapted for use with anhydrous ammonia. When ethylene dichloride is injected under pressure into a pressure system containing anhydrous ammonia at 150°C., needles of ethylenediamine hydrochloride are obtained, which on hydrolysis with alkali yield the free amine.[2]

When dilute aqueous ammonia is employed, the expected mixture of primary and polyamines is obtained. Thus, when 1,600 gm. of water, 340 gm. of anhydrous ammonia, and 200 gm. of ethylene dichloride are heated at 140 to 150°C. for approximately 1 hr., all the halide has entered into reaction. The product consists approximately of the following:

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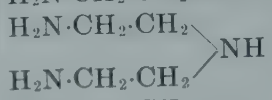
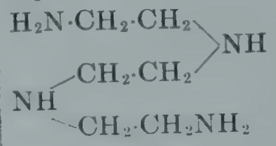
[1] Mills, U. S. 1,935,515 (1933).

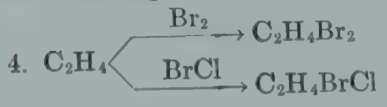
[2] Bersworth, U. S. 2,028,041 (1936).

Substance	B.p., °C.	Formula	%
Ethylenediamine	118	$H_2N{\cdot}CH_2{\cdot}CH_2NH_2$	40
Diethylenetriamine	208	 $\begin{matrix} H_2N{\cdot}CH_2{\cdot}CH_2 \\ H_2N{\cdot}CH_2{\cdot}CH_2 \end{matrix} \rangle NH$	30
Triethylenetetramine	266	 $\begin{matrix} H_2N{\cdot}CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{matrix} \rangle NH$ $NH \langle \begin{matrix} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2NH_2 \end{matrix}$	20
Higher polyamines	. . .	. . . .	10

Nafash has developed a cyclic process for the preparation of ethylenediamine and other primary alkylamines from the corresponding bromine derivatives.[1] A combination of well-known chemical reactions is employed, and these are indicated by the following equations:

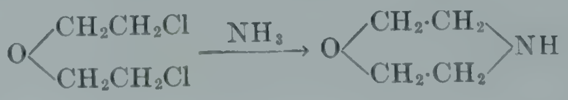
1. $C_2H_4Br_2 \xrightarrow{NH_3} C_2H_4(NH_2)_2{\cdot}2HBr$
2. $C_2H_4(NH_2)_2{\cdot}2HBr + 2NaOH \rightarrow C_2H_4(NH_2)_2 + 2NaBr + 2H_2O$
3. $2NaBr\ aq. + Cl_2 \rightarrow 2NaCl + Br_2$

3a. $NaBr\ aq. + Cl_2 \rightarrow NaCl + BrCl$

4.  $C_2H_4 \begin{cases} \xrightarrow{Br_2} C_2H_4Br_2 \\ \xrightarrow{BrCl} C_2H_4BrCl \end{cases}$

The alkyl bromides are more costly than the corresponding chlorine derivatives, and their use necessitates additional operating steps. These economic handicaps are to a substantial extent offset by certain advantages as follows: (1) the practicability of using weaker ammonia liquor; (2) the feasibility of operating at lower temperatures and pressures; and (3) the production of comparatively pure primary amines as the principal product.

Morpholine from β, β′ -dichlorodiethyl ether.



$$O \langle \begin{matrix} CH_2CH_2Cl \\ CH_2CH_2Cl \end{matrix} \xrightarrow{NH_3} O \langle \begin{matrix} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{matrix} \rangle NH$$

When the two chlorine atoms of *sym*-dichlorodiethyl ether are replaced by the imino group through the action of anhydrous ammonia, morpholine and dimorpholine are obtained. The synthesis is carried out by treating

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[1] Nafash, U. S. 2,075,825; 2,078,582 (1937).

sym-dichlorodiethyl ether dissolved in benzene with anhydrous ammonia at 50°.[1]

Preparation of Amino Acids.—When β-halogen acids are reacted with aqueous ammonia, unsaturated acids are formed, and very little amination occurs. The similar treatment of α-halogen acids leads not only to the corresponding primary amino acids but also to secondary and tertiary derivatives. In the ammonolysis of chloroacetic acid, the following products are obtained, the proportions depending largely on the ratio of aqueous ammonia:

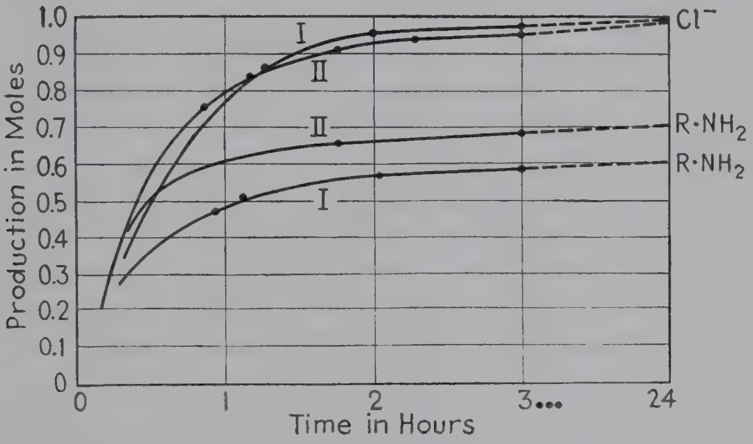
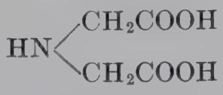


FIG. 4.—Ammonolysis of one mole chloroacetic acid. (*According to Cheronis.*)
I. Sixty moles of ammonia (aqueous) at 25°C
II. Four moles of ammonium carbonate at 60°C.

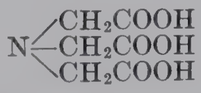
Glycine $H_2N \cdot CH_2COOH$

Diglycine



$$HN\begin{cases} CH_2COOH \\ CH_2COOH \end{cases}$$

Triglycine



$$N\begin{cases} CH_2COOH \\ CH_2COOH \\ CH_2COOH \end{cases}$$

To diminish the quantity of secondary and tertiary amines to less than 30 per cent, it is necessary to use a molar ratio $NH_3:CH_2ClCOOH$ of 60:1.

Cheronis has found that 4 moles of ammonium carbonate gives as good results as 60 moles of NH_3 *aq.* in the preparation of glycine.[2] The efficacy of these two agents is compared in Fig. 4. The difference between conversion and ammonolysis to primary amine indicates the extent of formation of di- and triglycine and glycolic acid—$CH_2OHCOOH$. The results obtained when the secondary and tertiary amines are reintroduced in subsequent batches have not been reported. A similar void in the literature exists regarding the conditions favorable for the maximum production of the polycarboxylic acid triglycine.

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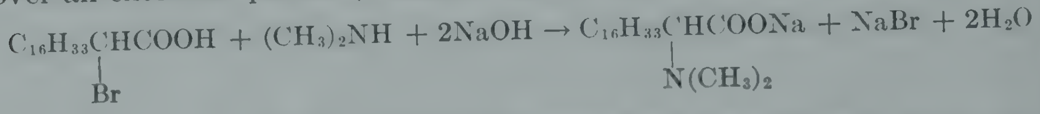
[1] Campbell, U. S. 2,034,427 (1937)

[2] CHERONIS and SPITZMUELLER, *J. Org. Chem.*, **6**, 349–375 (1941).

The conclusions that may be drawn from reaction-rate studies in the ammonolysis of halogen fatty acids are:

1. The reaction of most bromo acids with NH_3 *aq.* proceeds rapidly. Branched chains show a decrease in reactivity.
2. Ammonolysis of chloro acids, with the exception of chloroacetic, is not practical even with a 60 molar NH_3 ratio.
3. The rate of ammonolysis is increased by raising the temperature; and as is to be expected, this results in an increase in the amounts of secondary and tertiary amino derivatives as well as hydroxy compounds.

Long-chain monocarboxylic acids that contain 8 or more carbon atoms having an alpha halogen atom can also be converted to amino and alkylamino derivatives.[1] Thus, alpha bromostearic acid yields α-dimethylaminostearic acid when treated with aqueous dimethylamine dissolved in a 30 per cent sodium hydroxide solution. The reaction, which proceeds at room temperatures and atmospheric pressure and must be carried out over an extended period (6 days), may be represented as follows:



$$C_{16}H_{33}\underset{\displaystyle Br}{\underset{|}{C}}HCOOH + (CH_3)_2NH + 2NaOH \rightarrow C_{16}H_{33}\underset{\displaystyle N(CH_3)_2}{\underset{|}{C}}HCOONa + NaBr + 2H_2O$$

The sodium salt of the alkylamino fatty acid is soluble in water and hydrochloric acid and exhibits good foaming and detergent properties.

CLASS II. REPLACEMENT OF —SO_3H AND —OSO_3H GROUPS

Ammonolysis of Anthraquinonesulfonic Acids.—The replacement of the —SO_3H group by —NH_2 is limited to the anthraquinone series. The amination can be carried out readily at 165°C. with concentrated aqueous ammonia. Compared with the similar ammonolysis of halogenoanthraquinones, the reaction takes place at lower temperatures and purer amines can be obtained.

The need of oxidants in the ammonolysis of anthraquinonesulfonic acids has long been recognized. If it is not oxidized, the sulfurous acid that is split off gives rise to the formation of soluble reduction products. The yield of 2-aminoanthraquinone, according to the following reaction, is consequently only about 60 per cent of the theoretical.

$$C_{14}H_7O_2{\cdot}SO_3H + NH_3 \rightarrow C_{14}H_7O_2{\cdot}NH_2 + H_2SO_3$$

Lauer has found that inorganic oxidants have a specific value, depending on the particular anthraquinonesulfonic acid undergoing treatment as well as on the operating conditions employed.[2] Certain oxidants give rise to impurities that are not entirely removed by simple technical purification. When present even in traces, the impurities may interfere

[1] Henke and Schofield, U. S., 2,279,138 (1942).

[2] LAUER, *J. prakt. Chem.*, **135**, 7 (1932).

with the use of the amine in dyestuffs, this, in the final analysis, being the best criterion of purity.

The results obtained by Lauer in the ammonolysis of sodium anthraquinone-2-sulfonate are indicated by the curves in Fig. 5. When a mixture of sodium chlorate and ammonium nitrate was used as oxidants, yields of 90 to 94 per cent of a product of 99 per cent purity were obtained without the use of a copper catalyst.[1]

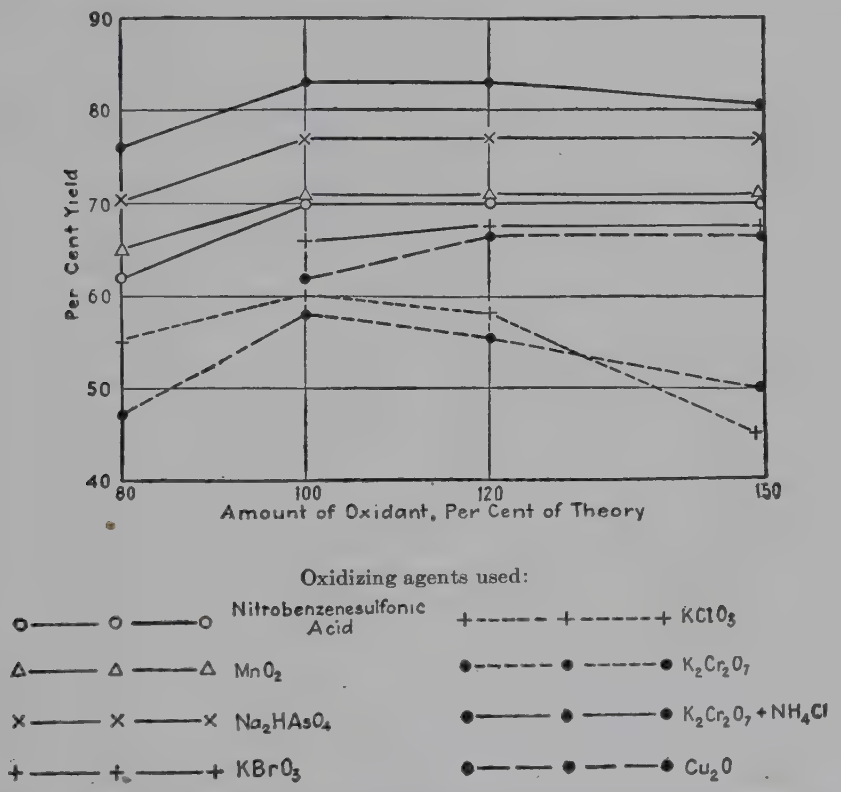


FIG. 5.—Effect of oxidants; ammonolysis of anthraquinone-2-sulfonic acid.

Ammonolysis of Aminoalkyl Hydrogen Sulfates.—Later, in discussing the replacement of —OH groups, it will be shown that when hydroxethanesulfonic (isethionic) acid is treated with ammonia, taurine is obtained by the preferential replacement of the hydroxyl group.

$$HOCH_2CH_2SO_3Na \xrightarrow[Na_2SO_3]{NH_3} H_2NCH_2CH_2SO_3Na$$

By contrast, the $—OSO_3H$ groups of aminoalkyl hydrogen sulfates can readily be replaced by reaction with ammonia or amines.[2] The reaction of ethanolamine with aminoethyl hydrogen sulfate thus yields hydroxyethyl-ethylenediamine.

$$H_2NC_2H_4OSO_3H + HOC_2H_4NH_2 \xrightarrow{NaOH} H_2NC_2H_4NHC_2H_4OH$$

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[1] GROGGINS and STIRTON, Unpublished research, 1935.

[2] Wilson, U. S., 2,364,178 (1944).

The simplest example of replacement of the $—OSO_3H$ group by an amino group is the preparation of ethylenediamine by the action of ammonia on aminoethyl hydrogen sulfate.

$$H_2NC_2H_4OSO_3H + NH_3 + 2NaOH \rightarrow H_2NC_2H_4NH_2 + Na_2SO_4 + 2H_2O$$

The products of reaction are not exclusively the di-primary amine but consist of the following related materials:

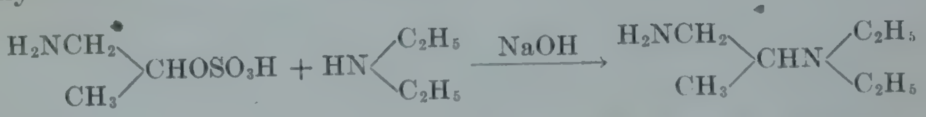
Products	Yield, %
Ethylenediamine	61.5
Diethylenetriamine	16
Tetra- and pentaethylene polyamines	9
Monoethanolamine	7
Hydroxyethyl-ethylenediamine	2
Total yield of amino compounds	95.5

It is clear that some hydrolysis occurs and an excess of mineral alkali is to be avoided. The recovered amino alcohols can, however, be converted readily to the corresponding aminoalkyl hydrogen sulfates for reuse.

When ethylenediamine replaces ammonia as the aminating agent, diethylenetriamine is the principal product.

$$H_2NC_2H_4OSO_3H + H_2NC_2H_4NH_2 \xrightarrow{NaOH} H_2NC_2H_4NHC_2H_4NH_2$$

Aminoisopropyl hydrogen sulfate behaves in a similar manner, and its reaction with diethylamine leads to the formation of aminoisopropyldiethylamine.



$$\begin{matrix}H_2NCH_2\\CH_3\end{matrix}\!\!>\!CHOSO_3H + HN\!<\!\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix} \xrightarrow{NaOH} \begin{matrix}H_2NCH_2\\CH_3\end{matrix}\!\!>\!CHN\!<\!\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$$

Aqueous ammonia or solutions of amines can be employed; and although a liberal excess of the aminating agent is used, some unconverted aminoalkyl hydrogen sulfate remains. This is converted to the alcohol by treatment with alkali, after which the product is distilled to remove water and the lower boiling amines. The higher amines are recovered by steam distillation and subsequently fractionated in another column. When ammonia is used as the aminating agent, satisfactory yields are obtained by carrying out the reaction at 130° for 5 hr. in an autoclave.

CLASS III. CONVERSION OF PHENOLS AND ALCOHOLS TO AMINES

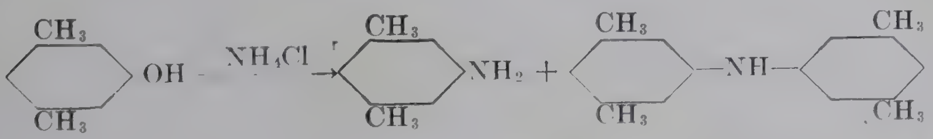
The pertinent type reactions listed at the beginning of this chapter indicate that the conversion of phenols and alcohols to amines by the action of ammonia may involve (1) the formation of a relatively stable alkali bisulfite addition compound, as in the Bucherer process; (2)

dehydration, as in the vapor- or liquid-phase treatment of alcohols in the presence of a dehydrating catalyst; and (3) reduction, as in the treatment of primary and secondary alcohols with hydrogen in the presence of a hydrogenation catalyst.

The catalytic ammonolysis of phenols and alcohols differs from the treatment of halogeno compounds in several respects. The compounds containing the —OH group are best aminated in the presence of metals preceding hydrogen in the electrochemical series. These active metals are, however, either ineffective or deleterious in the treatment of halogeno compounds, but copper-ammonia complexes are beneficial. In the replacement of halogen, the formation of the corresponding hydracid or its salts may lead to corrosion problems, whereas the treatment of compounds containing the —OH group involves the elimination of the elements of water which, as previously noted, is accomplished by diverse technics.

Conversion of Phenols to Amines.—When phenol and ammonia are heated under pressure in the presence of ferric chloride,[1] aluminum hydroxide, or ferrous hydroxide, aniline is obtained as the principal product[2] of amination, together with small proportions of diphenylamine. Ortho and para cresols can be treated similarly; but, as is well known, the corresponding amines can be obtained more economically by the direct reduction of nitrobenzene or appropriate nitrotoluenes.

sym-Xylenol (5-hydroxy-1, 3-dimethylbenzene) heated under pressure with ammonia yields the primary base as the main product, and this procedure is undoubtedly the best method of arriving at *sym*-xylidine. When this xylenol is heated under pressure to 320°C. with ammonium chloride, two products are obtained in approximately equal amounts. One is *sym*-xylidine (1-amino-3,-5-dimethylbenzene), and the other is *sym*-dixylylamine or 5-imino-bis-1, 3-dimethylbenzene:



Conversion of Naphthols to Naphthylamines. *Sulfurous Acid Salts as Catalysts* (*Bucherer Process*).—The most general method for the replacement of —OH by —NH$_2$ groups in naphthols is the use of ammoniacal solutions containing salts of sulfurous acid. The alkali metal bisulfites are ordinarily employed in the preparation of primary amines; but other compounds, such as the sulfite of methylamine $(CH_3{\cdot}NH_3)_2SO_3$, can be used in making substituted amines. As can be seen from the reaction mechanism below, the reaction is reversible and also permits the conversion of naphthylamines to naphthols.

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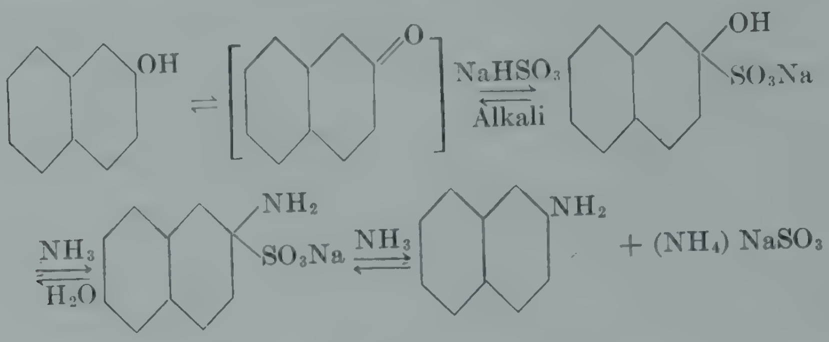
[1] Brit. 355,715 (1931).

[2] Brit. 386,375 (1932).



According to Fuchs and Stix, the formation of a naphthylamine from a naphthol, sodium bisulfite, and ammonia involves the addition of the bisulfite to the keto form of the naphthol.[1,2] The bisulfite (or sulfite) addition products of naphthols and naphthylamines are comparatively stable and, by adjusting the subsequent conditions of reaction, can be converted to either naphthols or naphthylamines. Compared with the corresponding naphthols, these addition compounds are more readily soluble in water. Those of monohydroxy compounds do not combine with diazo or tetrazo solutions, but those derived from some dihydroxy- and aminohydroxynaphthalenes still possess the power of combination, although in a lesser degree than do the dihydroxynaphthalenes and aminonaphthols themselves. Some of the aminonaphthol addition compounds can be diazotized, and the diazo compounds used in the manufacture of azo colors. The addition compounds are, in general, fairly stable against the action of dilute hydrochloric acid and sulfuric acid but are readily decomposed by alkali. They are hydrolyzed, however, on heating with concentrated sulfuric acid, yielding the corresponding hydroxy compounds. When heated with ammonia, they are converted into the amino derivatives.

It is, of course, unnecessary to prepare the intermediate addition compound first in order to prepare amino derivatives from the corresponding hydroxy compounds. By adding the reacting proportions of ammonium sulfite and providing sufficient ammonia, it is indeed entirely practical to go directly from hydroxy compound to amino derivatives or *vice versa.*

Sodium bisulfite may be substituted for the more costly ammonium salt without decreasing the yields of β-naphthylamine obtained by the

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[1] FUCHS and STIX, *Ber.*, **55**, 658 (1922).

[2] For a comprehensive review of the Bucherer reaction, the reader is referred to the contribution by DRAKE, "Organic Reactions," Vol. 1, John Wiley & Sons, Inc., New York, 1942.

Bucherer reaction.[1] In the course of the reaction, this is converted to the sodium ammonium salt in the presence of an excess of ammonia.

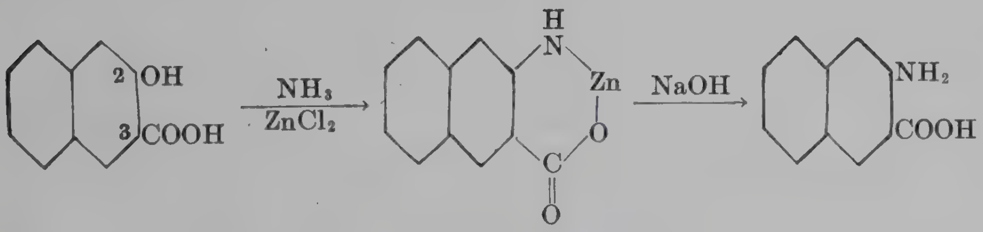
TABLE V.—AMINATION OF β-NAPHTHOL

Amination of 1 mole of β-naphthol, 8 hr. at 150°	1	2	3	4	5
Total H_2O in system, gm	475	475	475	475	475
Total NH_3 used, gm	28.4	31.8	35.2	37.8	44.55
NH_3 for amination, gm	25	25	25	25	25
NH_3 to form $NaNH_4SO_3$, gm	3.4	6.8	10.2	12.8	19.55
$NaNH_4SO_3$ used, moles	0.2	0.4	0.6	0.75	1.15
Yield of β-naphthylamine, *%	37	37	84	84	84

* Average results.

About 0.6 mole of sodium ammonium sulfite is necessary per mole of naphthol.

Preparation of 2-Aminonaphthalene-3-carboxylic Acid.—The ammonolysis of 2-hydroxynaphthalene-3-carboxylic acid affords an interesting study in the conversion of hydroxy compounds to amines, for it reveals a failure to appreciate the fundamental factors involved in this synthesis.



Fierz and Tobler recognized the advantages to be derived from the use of soluble salts of the more active metals—particularly zinc chloride because of its property of adding on ammonia—which had long been used in the amination of β-naphthol.[2] These salts are employed in quantities sufficient to form addition compounds or esters with the aromatic compounds. Instead of using zinc chloride, Schweitzer employs the zinc salt of the hydroxynaphthoic acid in the presence of ammonium chloride and Henle subsequently conceived the idea of incorporating zinc chloride-ammonia as the catalyst.[3,4] The operating details of the Fierz process are presented later in the technical section of this chapter.

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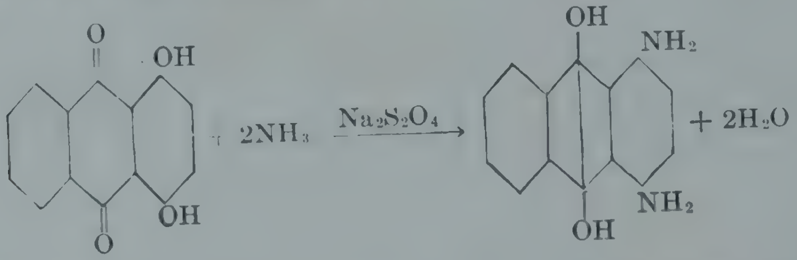
[1] BEZZUBEZ, *J. Chem. Ind. (Moscow)*, **7**, 908 (1932).

[2] FIERZ and TOBLER, *Helvetica Chim. Acta*, **5**, 557 (1922); U. S. 1,629,894 (1925).

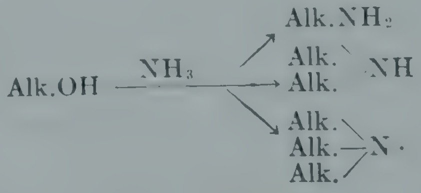
[3] Schweitzer, U. S. 1,806,714 (1931).

[4] Henle, U. S. 1,871,990 (1932).

Ammonolysis of Hydroxyanthraqninones.—The advantages of carrying out the ammonolysis of hydroxyanthraquinones in a reducing medium are illustrated in the preparation of 1, 4-diaminoanthraquinone from quinizarin.[1] When an aqueous solution containing $Na_2S_2O_4$ and quinizarin is treated with aqueous ammonia at 70 to 90°, leuco 1, 4-diaminoanthraquinone is formed, which can readily be oxidized to the quinone. The mono- and dialkylaminoanthraquinones are similarly prepared by employing an alkylamine instead of ammonia as the reactant.



Conversion of Alcohols.—Practically the whole range of primary alcohols from methanol and butanol to cetyl and octadecyl alcohols has been investigated. The synthesis of low-molecular-weight alkylamines from alcohols is almost always carried out in the vapor phase, according to the method of Sabatier and Mailhe in which the reacting alcohol and ammonia are passed over a dehydrating catalyst.[2] Compounds of aluminum or phosphorus; *e.g.*, alumina,[3] aluminum silicate,[4] aluminum phosphate,[5] and diammonium phosphate, are most frequently employed for this purpose. As in the amination of alkyl halides, the product of reaction may comprise primary, secondary, and tertiary amines, depending on the specific alcohol, the NH_3 ratio, and other conditions employed. The net reaction may be expressed thus:



The amines of the high-molecular-weight fatty acids are best prepared in a pressure system. Cetylamine is thus obtained by conducting cetyl alcohol and ammonia through a catalytic reaction chamber containing aluminum oxide which is kept at 380 to 400°C. and under a pressure of 125 atmos.[1] The vented vapors are condensed and yield an oily liquid containing some water. Upon distillation of the oil, cetylamine is obtained. Oleyl and stearyl alcohols react in a similar fashion. When alkylamines are employed instead of ammonia, the corresponding alkylamino compounds are formed. Thus, monoisobutyldodecylamine is prepared from 1 part *n*-dodecyl alcohol and 10 parts monoisobutylamine.[1] It is also possible to carry out the ammonolysis of the higher fatty alcohols in the vapor phase.[2] A mixture of primary, secondary, and tertiary amines is usually obtained.

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[1] U. S. 1,828,262 (1931).

[2] SABATIER, and MAILHE, *Compt. rend.*, **148,** 898 (1909).

[3] Arnold, U. S. 1,799,722 (1931); Reissue 19,632 (1935); SMOLENSKI, *Roczniki Chem.*, **1,** 232 (1921).

[4] Arnold, U. S. 1,799,722 (1931); Reissue 19,632 (1935); Martin and Swallen, U. S. 1,875,747 (1932).

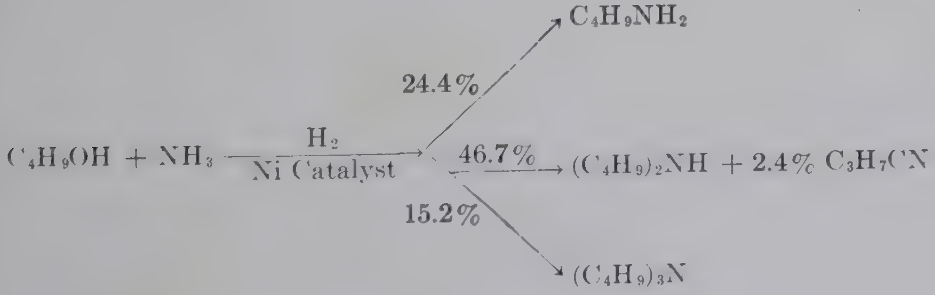
[5] Andrews, U. S. 2,073,671 (1937).

When the lower aliphatic alcohols are treated with ammonia in the vapor phase in the presence of a hydrogenation catalyst, nitriles are obtained as the principal product. Upon hydrogenation, these yield the corresponding amines, thus:

$$\text{Alk.CH}_2\text{OH} + \text{NH}_3 \xrightarrow[\text{Catalyst}]{\text{Ni}} \text{Alk.CN} \xrightarrow[\text{Ni Catalyst}]{\text{H}_2} \text{Alk.CH}_2\text{NH}_2$$

Olin and McKenna have found that the alkylamines can be obtained directly from the alcohols by carrying out the amination with ammonia in the presence of both hydrogen and a hydrogenation catalyst.[3] If the reaction proceeded via the formation of nitriles and subsequent hydrogenation, the exclusive or preponderant formation of primary amines would be expected in accordance with the reaction mechanism shown above. In practice, however, primary, secondary, and tertiary amines are obtained, as in the use of dehydrating catalysts. It is to be assumed, therefore, that the presence of hydrogen in conjunction with the hydrogenation catalyst establishes an equilibrium that prevents the appreciable formation of nitriles via a dehydrogenation process.

When butanol, ammonia, and hydrogen are passed through a pelleted nickel catalyst at 180°, the conversion to amines is 86.3 per cent and the following products are obtained.



$$\text{C}_4\text{H}_9\text{OH} + \text{NH}_3 \xrightarrow[\text{Ni Catalyst}]{\text{H}_2} \begin{cases} \xrightarrow{24.4\%} \text{C}_4\text{H}_9\text{NH}_2 \\ \xrightarrow{46.7\%} (\text{C}_4\text{H}_9)_2\text{NH} + 2.4\%\ \text{C}_3\text{H}_7\text{CN} \\ \xrightarrow{15.2\%} (\text{C}_4\text{H}_9)_3\text{N} \end{cases}$$

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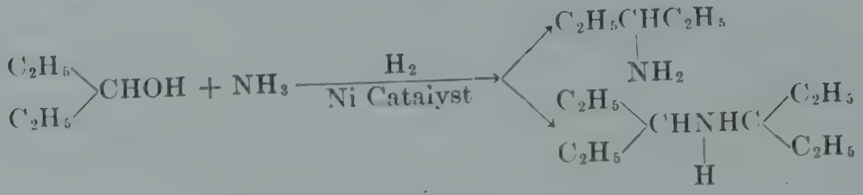
[1] Smeykal, U. S. 2,043,965 (1936).

[2] Arnold, U. S. 2,078,922 (1937).

[3] Olin and McKenna, U. S. 2,365,721 (1944).

Diethylcarbinol reacts similarly, and the products of reaction are



Taurine from Hydroxyethanesulfonic Acid (Isethionic Acid).

$$OH\cdot CH_2\cdot CH_2\cdot SO_3Na \xrightarrow[Na_2SO_3]{NH_3} H_2N\cdot CH_2\cdot CH_2\cdot SO_3Na$$

Taurine along with some ditaurine can be obtained by reacting 256 parts by weight of sodium hydroxyethanesulfonate with 800 parts of 25 per cent ammonia liquor at 210°C. for 3 hr. The addition of 10 parts of sodium sulfite aids materially in increasing the conversion, which falls off as the quantity of sodium sulfite is reduced. The synthesis is of particular interest, because it shows that in aliphatic compounds containing both sulfonic and hydroxyl groups, the —OH group can be replaced preferentially by $—NH_2$ and $—N\begin{matrix}\diagup Alk\\ \diagdown H\end{matrix}$[1,2]. In addition to sodium sulfite, other salts such as sodium carbonate can be used. In the preparation of the alkylamino derivatives, *e.g.*, methyltaurine, the introduction of caustic potash is found to be advantageous.

CLASS IV. CONVERSION OF CARBONYL COMPOUNDS

The conversion of aldehydes and ketones to amines by the action of ammonia or amines is carried out in the presence of hydrogen and a hydrogenation catalyst. The reactions involving the lower aliphatic aldehydes usually take place in the vapor phase, whereas the treatment of high-boiling aldehydes, aldose sugars, or ketones is generally effected in the liquid phase. In liquid-phase reactions, better results are obtained if the conjoint amination reduction is carried out under pressure in the presence of an alcohol as a diluent or solvent.

Anhydrous ammonia, either as a liquid or a gas, is the preferred aminating agent for the preparation of primary amines, although concentrated aqueous ammonia can be satisfactorily employed in some liquid-phase reactions. Nickel catalysts are generally used in conjunciton with hydrogen to effect the reduction of the carbonyl group.

When unsaturated aliphatic aldehydes such as acrolein are treated,

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[1] Nicodemus and Schmidt, U. S. 1,999,614 (1935).

[2] Nicodemus and Schmidt, U. S. 1,932,907 (1933).

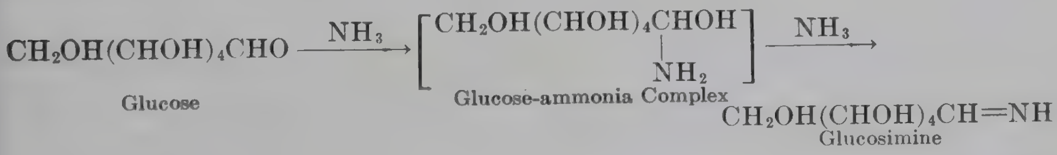
saturation as well as amination occurs, and a normal primary amine is obtained.

Conversion of Aldehydes.—Saturated and unsaturated aliphatic aromatic aldehydes can be converted to amines in the vapor phase by passing their vapors along with equal volumes of ammonia and hydrogen over a heated nickel catalyst.[1] A reaction temperature of 125 to 150°C. has been found satisfactory. To avoid resinification of unstable unsaturated aldehydes or ketones before their contact with the catalyst, they are preferably vaporized separately, and their vapors, admixed with fresh hydrogen, are led into the reaction system where they are mixed with the circulated, preheated mixture of ammonia and hydrogen. The ammonolysis of acrolein and crotonaldehyde, is as follows:

$$\underset{\text{Acrolein}}{CH_2{:}CH{\cdot}CHO} \xrightarrow[H_2]{NH_3} \underset{n\text{-Propylamine}}{CH_3{\cdot}CH_2{\cdot}CH_2NH_2}$$

$$\underset{\text{Crotonaldehyde}}{CH_3{\cdot}CH{:}CH{\cdot}CHO} \xrightarrow[H_2]{NH_3} \underset{n\text{-Butylamine}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2NH_2}$$

Amination of Aldose Sugars.—The action of ammonia and amines on aldose sugars may lead to diverse products depending on the conditions employed. The simple addition of ammonia results in the formation of the aldehyde-ammonia addition compound of the aldose sugar. The condensation product formed by the elimination of water is the aldosimine. The conversion of glucose to glucosimine is shown by the following equation.



$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow{NH_3} \underset{\text{Glucose-ammonia Complex}}{\left[\begin{array}{l} CH_2OH(CHOH)_4\underset{\displaystyle NH_2}{\underset{|}{CHOH}} \end{array}\right]} \xrightarrow{NH_3} \underset{\text{Glucosimine}}{CH_2OH(CHOH)_4CH{=}NH}$$

The aldosimines are best prepared by the use of substantially anhydrous ammonia and a solvent such as methanol.[2] Practically complete conversion of the aldose sugars—glucose, lactose, and xylose—can be obtained at amination temperatures of 60 to 80°.

The reaction of aldose sugars with aqueous ammonia or alkylamine in the presence of hydrogen and a hydrogenation catalyst leads to the formation of the aldosamines.[3] The conjoint amination reduction may be expressed as follows:

$$CH_2OH(CHOH)_4CHO \xrightarrow[Ni]{NH_3 + H_2} CH_2OH(CHOH)_4CH_2NH_2 + H_2O$$

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[1] Kauter, U. S. 2,051,486 (1936).

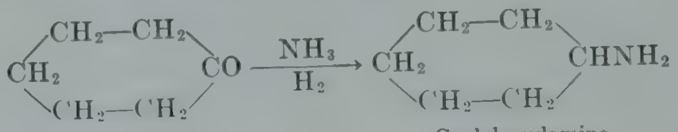
[2] Lorand, U. S. 2,235,938 (1941).

[3] Flint and Salzberg, U. S. 1,994,467; 2,016,963 (1935).

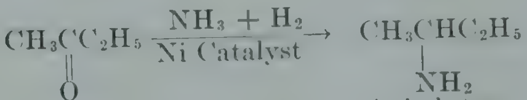
The preparation of the primary aldosamines can be effected with concentrated aqueous ammonia at temperatures from 65 to 95°. The reaction products are viscous noncrystalline sirups, which can be crystallized out of methanol to give stable hydroxyamino compounds.

Conversion of Ketones.—The conversion of ketones to amines can be carried out in either the vapor or liquid phase. The technic employed depends on the physical and chemical properties of the reactants and final products. The conjoint use of ammonia and hydrogen in the presence of a hydrogenation catalyst is necessary.

The intranuclear ketone, cyclohexanone, can be converted advantageously in the vapor phase to cyclohexylamine.[1] The preparation of 2-aminobutane from methyl ethyl ketone (butanone-2) and of 12-aminostearamide from the corresponding keto amide are, however, best carried out in the liquid phase. The pertinent reactions are

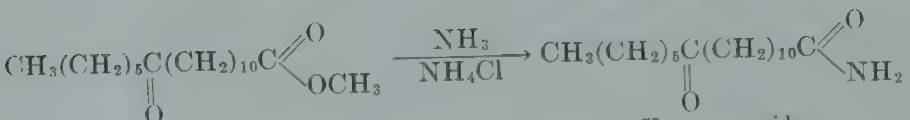


Cyclohexylamine



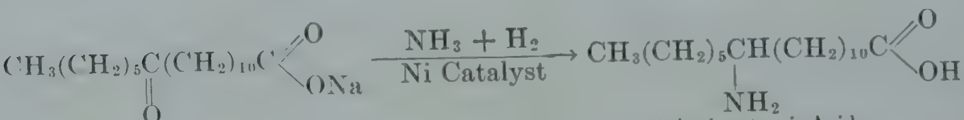
$$\underset{\overset{\|}{O}}{CH_3CC_2H_5} \xrightarrow[\text{Ni Catalyst}]{NH_3 + H_2} \underset{\overset{|}{NH_2}}{CH_3CHC_2H_5}$$

2-Aminobutane



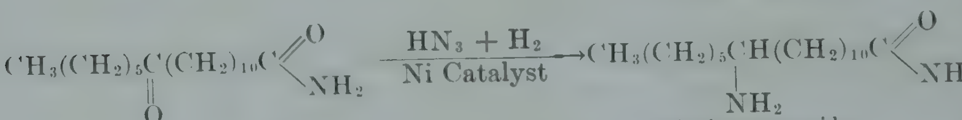
$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OCH_3} \xrightarrow[NH_4Cl]{NH_3} CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow NH_2}$$

12-Ketostearamide



$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow ONa} \xrightarrow[\text{Ni Catalyst}]{NH_3 + H_2} CH_3(CH_2)_5\underset{\overset{|}{NH_2}}{CH}(CH_2)_{10}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$$

12-Aminostearic Acid



$$CH_3(CH_2)_5\underset{\overset{\|}{O}}{C}(CH_2)_{10}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow NH_2} \xrightarrow[\text{Ni Catalyst}]{HN_3 + H_2} CH_3(CH_2)_5\underset{\overset{|}{NH_2}}{CH}(CH_2)_{10}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow NH_2}$$

12-Aminostearamide

The amination of butanone-2 is best carried out in the presence of an alcoholic solvent. Without the use of an alcohol, yields of 65 per cent are obtained. The use of tert-butyl alcohol results in a yield of 85.8 per cent, and the employment of butanol-2 gives a 91 per cent yield. It is to be recalled, however, that butanol-2, like butanone-2, can also be converted to 2-aminobutane under comparable operating conditions.[2]

The ketostearins are converted to ketostearamides when treated with anhydrous ammonia and small amounts of ammonium chloride. When the amination takes place in the presence of hydrogen and a nickel catalyst, the keto acids and keto amides are converted to the corresponding amino compounds. In the treatment of the keto acids, it is desirable to add sufficient alkali and water to form the alkali soap.

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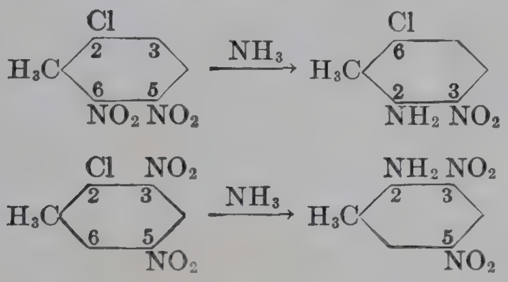
[1] Kauter, U. S. 2,051,486 (1936).

[2] Olin, U. S., 2,278,372; 2,278,373; 2,365,721 (1944).

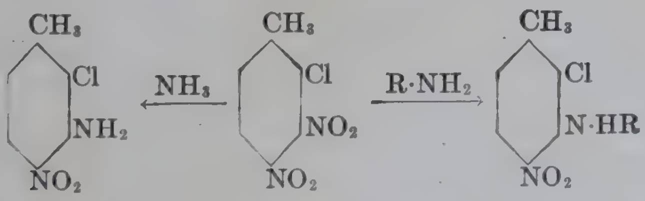
CLASS V. REPLACEMENT OF LABILE NITRO GROUPS

Before concrete examples of the type reactions of this group are given, it is advisable to draw attention to a peculiar but important property that attaches to the arrangements of nitro groups in cyclic compounds. Whenever a nitro group is found ortho or para to another nitro radical, it is rendered labile or very susceptible to chemical action. This mobility offers a convenient method of making transformations otherwise very difficult. Thus, Kenner and Parkin obtained 3-nitro-*o*-toluidine from 2, 3-dinitrotoluene by treating the latter with alcoholic ammonia for 15 hr. at 150 to 160°C.[1]

When 5, 6-dinitro-*o*-chlorotoluene is treated with alcoholic ammonia under pressure, the reaction product obtained is 6-chloro-3-nitro-*o*-toluidine. If however, 3, 5-dinitro-*o*-chlorotoluene is thus treated, the halogen is replaced and 3, 5-dinitro-*o*-toluidine is produced. The group ortho to the nitro substituent is in each case the one entering into the reaction.



In fact, the replacement of the labile nitro group takes place so readily that it can be replaced quantitatively by bases.[2] Thus, when 2-chloro-3, 4-dinitrotoluene is treated with ammonia or aniline, the following substituted toluidines are obtained:



Burton and Kenner ascertained that the nitro group that suffers replacement under the influence of alcoholic ammonia would be more resistant to the action of reducing agents; thus, 3- 4-dinitro-*o*-xylene gives 3-nitro-*o*-4-xylidine when treated with alcoholic ammonia, whereas 4-nitro-*o*-3-xylidine was obtained by reduction with stannous chloride.[1]

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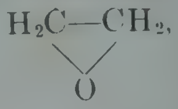
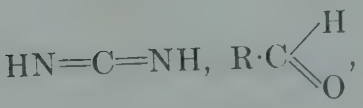
[1] KENNER and PARKIN, *J. Chem. Soc.* **117**, 852 (1920).

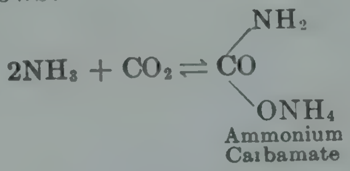
[2] MORGAN and GLOVER, *J. Chem. Soc.*, **119**, 1700 (1921).

CLASS VI. ADDITION REACTIONS

As would be expected, the formation of amines by addition reactions is confined to highly reactive compounds, such as $O{=}C{=}O$,  $H_2C{-}CH_2$ with O bridging,  $HN{=}C{=}NH$, $R{\cdot}C\begin{smallmatrix}H\\ \| O\end{smallmatrix}$, $HC{\equiv}CH$, and $CH_2{=}CHC{\equiv}N$. Frequently, the primary addition compound is so unstable or reactive that secondary reactions occur before a stable amine is obtained. In some instances, as in the preparation of guanidine, it is necessary to introduce an ammonium salt to inhibit further reaction.

The Synthesis of Urea from CO_2.—Although urea was the first of the organic compounds to be formed synthetically, its commercial production had to await the development of the synthetic ammonia process. Here the principal product, NH_3, and a by-product, CO_2, which constitute the raw materials for urea production, are prepared cheaply.

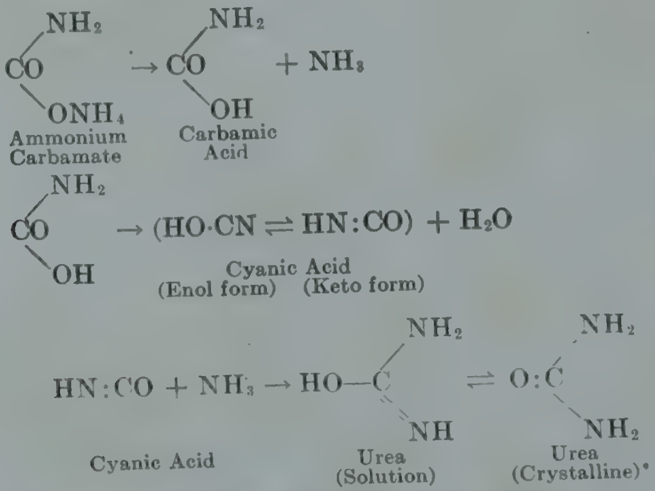
The reactions involved in the formation of urea from carbon dioxide and ammonia are as follows:



$$2NH_3 + CO_2 \rightleftharpoons CO\begin{matrix}NH_2\\ ONH_4\end{matrix}$$

Ammonium Carbamate

At elevated temperatures, urea is formed from ammonium carbamate by a series of reactions:



$$CO\begin{matrix}NH_2\\ ONH_4\end{matrix} \rightarrow CO\begin{matrix}NH_2\\ OH\end{matrix} + NH_3 \qquad (1)$$

Ammonium Carbamate, Carbamic Acid

$$CO\begin{matrix}NH_2\\ OH\end{matrix} \rightarrow (HO{\cdot}CN \rightleftharpoons HN{:}CO) + H_2O \qquad (2)$$

Cyanic Acid (Enol form) (Keto form)

$$HN{:}CO + NH_3 \rightarrow HO{-}C\begin{matrix}NH_2\\ NH\end{matrix} \rightleftharpoons O{:}C\begin{matrix}NH_2\\ NH_2\end{matrix} \qquad (3)$$

Cyanic Acid, Urea (Solution), Urea (Crystalline)[2]

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[1] BURTON and KENNER, *J. Chem. Soc.*, **119**, 1047 (1921).

[2] HENDRICKS, *J. Am. Chem. Soc.*, **52**, 3088 (1930).

Although the transformation of ammonium carbamate to urea is not a direct dehydration, the presence of water is, however, a limiting factor with respect to the extent that the reaction occurs. It has been found that at any temperature, a definite equilibrium is established that can be approached from either direction.[1] Krase and Gaddy have shown that a real shift in the carbamate-urea-water equilibrium is obtained by employing an excess of anhydrous ammonia, which functions as a strong dehydration agent.[2] The employment of ammonia, up to 280 per cent of that combined as carbamate, gives conversions to urea between 81 and 85 per cent of the carbamate ammonia. These results are shown in the curve of Fig. 6,

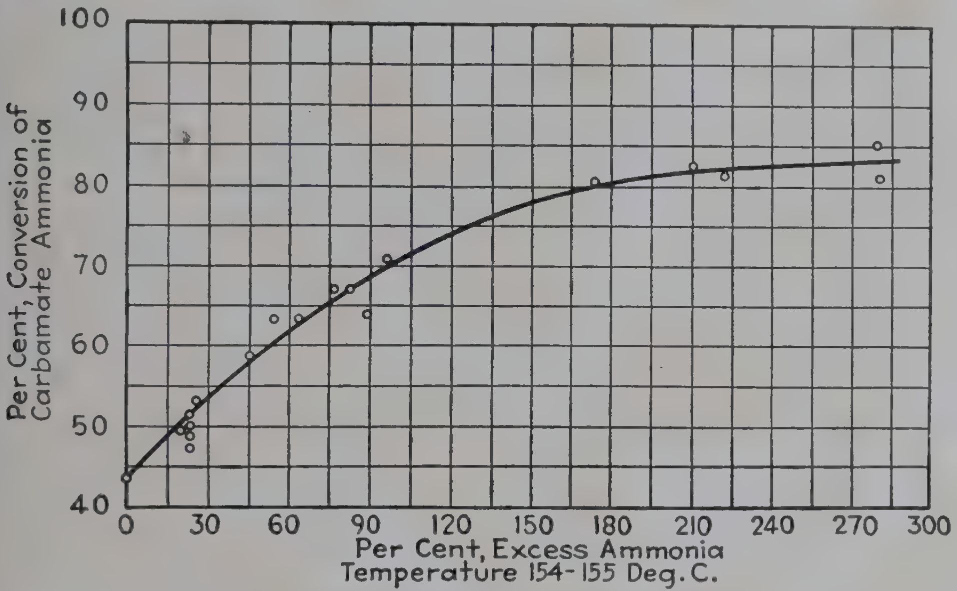
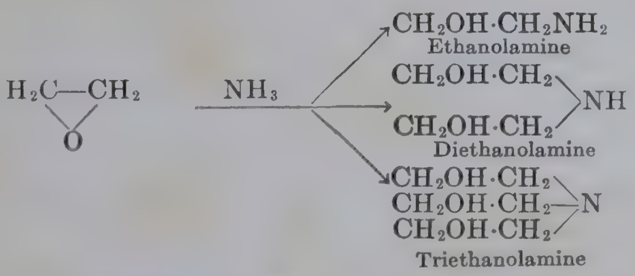


FIG. 6.—Effect of NH_3 ratio on urea formation.

The Conversion of Alkylene Oxides to Alkanolamines.—The alkylene oxides, *e.g.*, ethylene,[3] isopropylene,[3,4] and isobutylene[4] oxides can readily be converted to alkanolamines.


H₂C—CH₂
O
NH₃
CH₂OH·CH₂NH₂
Ethanolamine
CH₂OH·CH₂
NH
CH₂OH·CH₂
Diethanolamine
CH₂OH·CH₂
CH₂OH·CH₂—N
CH₂OH·CH₂
Triethanolamine

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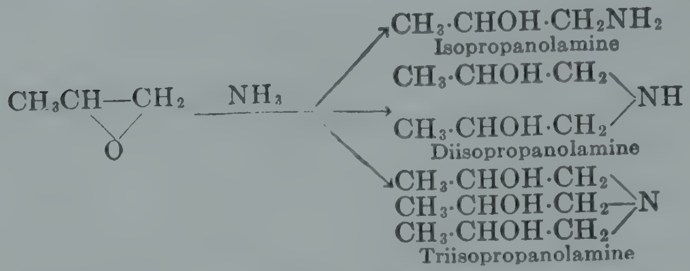
[1] Clark, Gaddy, and Rist, *Ind. Eng. Chem.*, **25**, 1092 (1933).

[2] Krase and Gaddy, *J. Am. Chem. Soc.*, **52**, 3088 (1930).

[3] Kauter, U. S. 2,051,486 (1936).

[4] Wickert, U. S. 1,988,225 (1935).

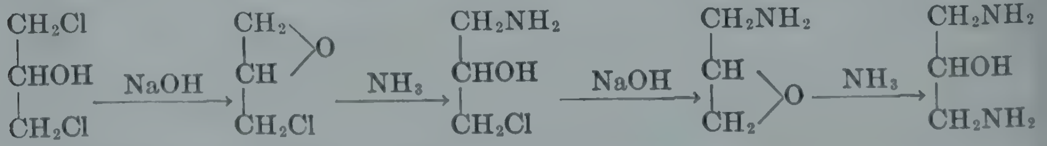

CH₃CH—CH₂
O
NH₃
CH₃·CHOH·CH₂NH₂
Isopropanolamine
CH₃·CHOH·CH₂
NH
CH₃·CHOH·CH₂
Diisopropanolamine
CH₃·CHOH·CH₂
CH₃·CHOH·CH₂
N
CH₃·CHOH·CH₂
Triisopropanolamine

These reactions are exothermic, and an operating temperature of 50° to 60°C. usually suffices. When ordinary 28 per cent aqueous ammonia is employed, primary, secondary, and tertiary amines are obtained—the proportions being dependent on the NH_3 ratio.

When propylene oxide is bubbled into aqueous ammonia at 40 to 50°C. in a sealed agitated vessel, the isopropanolamines are formed, and these can be separated by fractional distillation. Wickert has shown that it is feasible to control the proportions of the various amines by adjusting the relative concentration of the reactants.[1] The curves in Fig. 7 show clearly the relation of the reactants to the products. The physical properties of the ethanol- and propanolamines, which find employment as wetting agents and rubber accelerators and as absorbents for acidic gases, are given below.[1]

Substance	Sp. gr., 20°/20°C.	B.p. at 5 mm., °C.	Freezing point, °C.	1 % solution, alkalinity pH
Monoisopropanolamine	0.981	45	−5	11.4
Diisopropanolamine	1.0089	116	32	11.1
Triisopropanolamine	1.0196	144	45	10.2
Monoethanolamine	1.0180	58	10.5	11.50
Diethanolamine	1.0984	156	28.0	11.75
Triethanolamine	1.1258	201	21.2	11.30

In contrast to the alkylene oxides which on ammonolysis give rise to amines with one to three alkanol groups, the epichlorohydrins derived from allyl chloride or glycerol yield diaminopropanol. When 1 mole of 1, 3-dichloropropanol-2 is added to 2 liters of aqueous ammonia containing 2 moles of NaOH at 30 to 50°C., the conversion to diamine takes place according to the following scheme.[2]


CH₂Cl
CHOH
CH₂Cl
NaOH
CH₂
CH
O
CH₂Cl
NH₃
CH₂NH₂
CHOH
CH₂Cl
NaOH
CH₂NH₂
CH
O
CH₂
NH₃
CH₂NH₂
CHOH
CH₂NH₂

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[1] Wickert, U. S. 1,988,225 (1935).

[2] Bottoms, U. S. 1,985,885 (1935); 2,065,113 (1936); Eisleb, U. S. 1,790,042 (1931).

The first reaction that takes place probably is one between the dichlorohydrin and the caustic soda in which one chlorine atom is removed with the formation of epichlorohydrin. This immediately reacts with a molecule of ammonia to form a glyceryl aminochlorhydrin, which then reacts with caustic soda forming sodium chloride, releasing water and producing epiaminohydrin. The epiaminohydrin forthwith reacts with a further quantity of ammonia to produce the 1, 3-diaminopropanol-2. The intermediate formation of epihydrins makes it necessary to have ammonia present in large excess and at the operating temperature (50°C.) in order to prevent the amino derivatives that are first formed from reacting with further quantities of the chlorhydrin and producing secondary and tertiary amines and complex polymers.

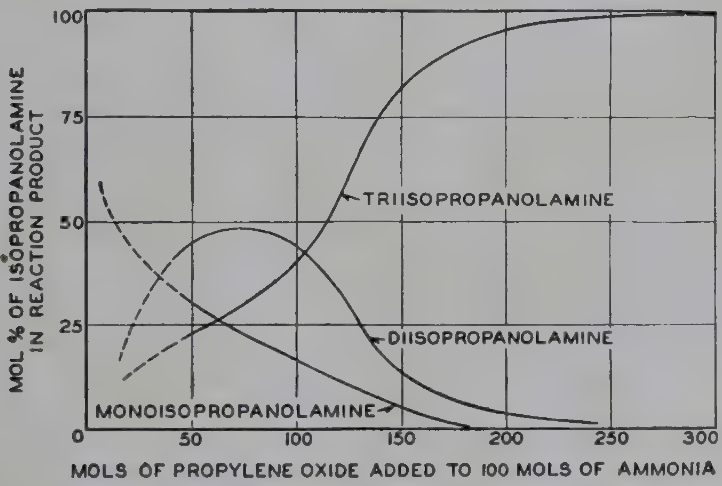

Fig. 7.—Preparation of propanolamines; influence of NH_3 ratio.

β-Alanine from Acrylonitrile.—The amino group cannot be added directly to alkenes or doubly bound carbon atoms of fatty acids, such as oleic acid, by the action of ammonia. Such compounds must first be converted to halides or other derivatives susceptible to ammonolysis. When, however, the double bond is conjugated with a C≡N group, addition of ammonia occurs and a saturated beta amine is formed. Acrylonitrile can thus be converted to aminopropionitrile, which on hydrolysis with aqueous ammonia at 200° yields β-alanine, an important intermediate in the preparation of pantothenic acid.[1]

$$CH_2{=}CHC{\equiv}N + NH_3\,aq \rightarrow H_2NCH_2CH_2CN \xrightarrow{NH_3\,aq.} H_2NCH_2CH_2COOH$$

There is as yet no direct evidence of the mechanism of addition of bases to such conjugated unsaturated systems. It is known that unsaturated ketones $\left(\overset{4}{C}{=}\overset{3}{C}{-}\overset{2}{C}{=}\overset{1}{O}\right)$ in general undergo 1-2, 3-4, and 1-4 additions. The product of addition, however, is not always determined by the relative rates of two competing reactions.[1] In fact, it seems probable—particularly in the reaction under consideration—that the relative stability of the products resulting from competing reactions is of major importance. The highly polar $\overset{+}{C}{=}O$ or $\overset{+}{C}{\equiv}N$ group would be expected to confer electrophylic (*i.e.*, electron-accepting) character on the olefin carbon atom 4 by electromeric relay, as follows:[2] $\overset{4}{C}H_2{=}\underset{\curvearrowright}{\overset{3}{C}H}.\overset{2}{C}\underset{\curvearrowright}{\equiv}\overset{1}{N}$.

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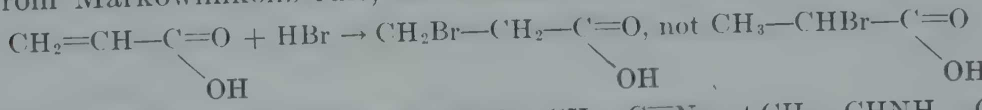
[1] Carlson and Hotchkiss, U. S. 2,377,401 (1945).

The effect of conjugation of a C=C with a C=O or C≡N bond would be to permit the formation of addition products that would not be expected from Markowinikoffs rule, as is evidenced by the following reactions:[3]



$$CH_2{=}CH{-}C({=}O){-}OH + HBr \rightarrow CH_2Br{-}CH_2{-}C({=}O){-}OH,\ \text{not}\ CH_3{-}CHBr{-}C({=}O){-}OH$$

$$CH_2{=}CH{-}C{\equiv}N + H{\cdot}NH_2 \rightarrow H_2NCH_2{-}CH_2{-}C{\equiv}N,\ \text{not}\ CH_3{-}CHNH_2{-}C{\equiv}N$$

According to Cromwell, it appears logical that the driving force for the addition of $H{\cdot}NH_2$ to acrylonitrile is the attraction of the electrophylic carbon atom 4 for the unshared electrons of the ammonia nitrogen.[4] It is consequently reasonable to presume that the formation of aminopropionitrile as an intermediate compound in the synthesis of beta alanine is due to the direct attack of the unshared electrons of $:NH_3$ at the electron-deficient carbon atom 4.[5]

A similar addition reaction occurs when an acrylic acid ester, such as methyl acrylate, is treated under pressure with aqueous ammonia.[6] Hydrolysis and ammonolysis occur, and beta alanine is formed.

$$CH_2{=}CHCOOCH_3 \xrightarrow{NH_3\ aq.} H_2NCH_2CH_2COOH$$

Whether the intermediate product is acrylic acid or acrylamide has not been reported.

From the available information, it appears that the yields of beta-alanine from methyl acrylate are considerably greater than those resulting from the ammonolysis of either cyanhydrin or acrylonitrile.

Guanidine from Cyanamide.—Ammonia adds to cyanamide to form guanidine. It is presumed that addition occurs at the —C≡N group with the formation of the amidine.

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[1] Cromwell, *Chem. Rev.*, **38**, 83–137 (1946).

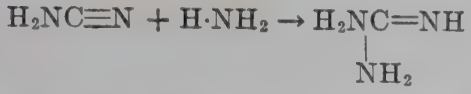
[2] Remick, "Electronic Interpretation of Organic Chemistry," p. 123, John Wiley and Sons, Inc,, New York (1943).

[3] Branch and Calvin, "The Theory of Organic Chemistry," p. 469, Prentice-Hall, Inc., New York (1941).

[4] Cromwell, University of Nebraska, private communication.

[5] The mechanism of β-alanine formation from other types of nitriles may be explained in fundamentally the same manner. $R{-}O{-}CH_2{-}CH_2{-}C{\equiv}N \rightarrow R{-}O{-}H + H_2N{-}CH_2{-}CH_2{-}C{\equiv}N$, where R represents H, alkyl or $-CH_2{-}CH_2{-}CN$.

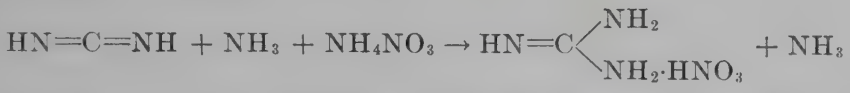
[6] Babcock and Baker, U. S. 2,376,334 (1945).



$$H_2NC\equiv N + H\cdot NH_2 \rightarrow H_2NC(=NH)NH_2$$

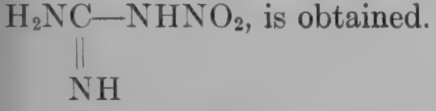
In practice, the ammonolysis is carried out in the presence of ammonium salts—preferably ammonium nitrate—and the comparatively stable guanidine nitrate is formed. Such a technic is employed to prevent the relatively active guanidine from combining with unreacted cyanamide to form melamine. The reaction is carried out by heating cyanamide or dicyandiamide with ammonia and ammonium nitrate for 2 hr. at 160° under autogenic pressure. During the course of the reaction, dicyandiamide is formed from cyanamide in the presence of ammonia and, in all probability, is the primary product.

The monomeric reaction is



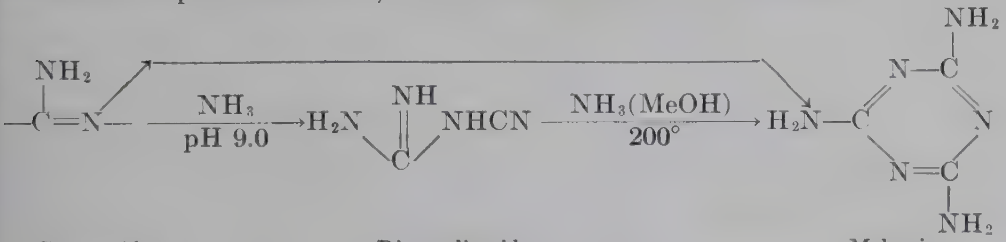
$$HN{=}C{=}NH + NH_3 + NH_4NO_3 \rightarrow HN{=}C(NH_2)(NH_2\cdot HNO_3) + NH_3$$

Upon removal of the elements of water with concentrated sulfuric acid the important military and industrial explosive nitroguanidine, $H_2NC(=NH)—NHNO_2$, is obtained.



$$H_2NC(=NH)—NHNO_2$$

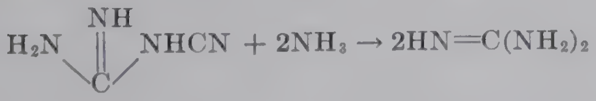
Dicyandiamide and Melamine from Cyanamide.—Cyanamide solutions are stable when slightly acid and are polymerized when slightly alkaline. Thus, when cyanamide or dicyandiamide is heated in the presence of liquid ammonia, the triazine melamine is formed.



Cyanamide Dicyandiamide Melamine

It is believed that part of the cyanamide or dicyanamide first reacts with ammonia to form guanidine according to the following equations.[1]

$$H_2N\overset{+}{C}\equiv\overset{-}{N} + \overset{+}{H}\cdot\overset{-}{N}H_2 \rightarrow HN{=}C(NH_2)_2 \qquad (1)$$



$$H_2N\text{—}C(=NH)\text{—}NHCN + 2NH_3 \rightarrow 2HN{=}C(NH_2)_2 \qquad (2)$$

The relatively reactive guanidine combines with unreacted starting material to form melamine with the regeneration of ammonia.

$$HN{=}C(NH_2)_2 + 2H_2NC\equiv N \rightarrow (H_2NCN)_3 + NH_3 \qquad (3)$$

$$HN{=}C(NH_2)_2 + (H_2NC\equiv N)_2 \rightarrow (H_2NCN)_3 + NH_3 \qquad (4)$$

---

[1] Hill, Swain, and Paden, U. S. 2,252,400 (1941).

To obviate such polymerizing reactions, it is necessary to introduce the nitrate or other acidic radicals as a coreactant. The initially formed guanidine is consequently bound as a stable salt which is no longer free to combine with further amounts of cyanamide.

The efficient conversion of cyanamide to the dimer depends on the control of the pH and the use of relatively concentrated solutions. The effect of hydrogen-ion concentration on the formation of dicyandiamide has been studied by numerous investigators, and it is generally agreed that the pH should be between 8.6 and 9.9[1] The maximum reaction rate appears to be at pH 9.2 at 82° and slightly higher at lower temperatures.

Numerous side reactions are possible and do occur, even under closely controlled conditions. Some of the impurities that are present after polymerization are urea, guanidine, melamine, ammeline, and ammelide. The total combined amount of these substances after a single polymerization is not great; but in continuous operations where mother liquors from the crystallization of dicyandiamide are recirculated for further extraction of cyanamide (see technical section), there is a steady increase in the concentration of such by-products. It is necessary therefore, to discard some of the mother liquor regularly in order to avoid contamination of the dicyandiamide and to obviate operating difficulties.

Pinck and Hetherington showed that the maximum conversion of cyanamide to dicyandiamide is obtained when the starting solution

TABLE VI.—POLYMERIZATION OF CYANAMIDE SOLUTIONS WITH VARYING CONCENTRATIONS OF CYANAMIDE AND AMMONIA

Conc. of initial solution			Analysis of product			
Expt. No.	Cyanamide, %	NH_3, %	Total N, gms.	Ammonia N, gm.	Dicyanodiamide N, gm.	Conversion, %
1	38.0	0.6	1.446	0.001	0.766	53.0
2	38.0	2.4	1.924	0.004	1.228	95.2
3	38.0	4.5	1.252	0.009	1.195	96.2
4	21.7	0.6	0.734	0.001	0.381	51.9
5	21.7	2.4	0.708	0.003	0.680	96.6
6	21.7	4.5	0.700	0.004	0.671	96.5
7	10.0	0.6	0.351	0.003	0.039	10.8
8	10.0	2.4	0.365	0.004	0.110	30.6
9	10.0	4.5	0.395	0.006	0.204	52.3*

* Cyanamide nitrogen, 0.182 gm. or 46.8 per cent.

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[1] COCHET, *Congres des Engrais Azates de Synthese*, May, 1927; BUCHANAN and BARSKY, *J. Am. Chem. Soc.*, **52**, 195 (1930); BARSKY, *News Ed. Am. Chem. Soc.*, **18**, 759 (1940); PINCK and HETHERINGTON, *Ind. Eng. Chem.*, **27**, 834 (1935); BAUGHEN, *Can. Chem. Process Ind.*, **28**, 805 (1944).

contains at least 20 per cent cyanamide and 2 per cent ammonia (Table VI).[1] Cyanamide is quantitatively polymerized to the dimer in liquid ammonia solution upon spontaneous evaporation of the solvent. The use of ammonia is, however, not essential inasmuch as cyanamide polymerizes readily in alkaline solution; and in commercial practice, the batch is "set" at the optimum pH, *viz.*, about 9.2 at 180°.

Crystalline cyanamide (m.p., 42°), when heated to 150°, polymerizes with explosive violence to melamine or 2, 4, 6-triamino-1, 3, 5-triazine. In practice, the trimer is obtained from the dimer, dicyandiamide by heating with ammonia. Scholl and Davis obtained melamine as the principal product by heating dicyandiamide with 2 parts of liquid ammonia at 155° for 2 hr.[2] Subsequent research showed that economies in the use of ammonia could be realized by carrying out the reaction at higher temperatures[3] (380°) or in the presence of a solvent such as methanol.[4] When ammonium chloride is used instead of ammonia, the product contains guanidine hydrochloride in addition to melamine, the quantity of guanidine salt being approximately proportional to the molar ratio of ammonium chloride to cyanamide. The ammonia liberated during the guanidine synthesis serves to catalyze the polymerization reaction.

IV. PHYSICAL AND CHEMICAL FACTORS AFFECTING AMMONOLYSIS

A number of factors accelerate or retard the replacement of atoms or radicals by the amino group. These will be discussed in the following order: (1) solubility; (2) agitation; (3) halogen derivative treated; (4) presence of nitro groups; (5) temperature of amination and NH_3 concentration; and (6) free space in autoclaves.

Solubility.—The soluble anthraquinonesulfonic acids are more readily converted to amines than the insoluble halogeno compounds. A similar comparison cannot be drawn, however, between 4′-chloro-2-benzoylbenzoic acid and the 2-chloroanthraquinone derived from it upon ring closure. In the soluble keto acid, the halogen is attached to the benzene nucleus, and it is consequently more difficult to replace than the chlorine atom linked to the anthraquinone nucleus. It is thus absolutely necessary to employ a metal catalyst in the ammonolysis of the halogeno keto acid, whereas its use in the conversion of the anthraquinone derivative is not essential, although the use of a copper compound accelerates the reaction.

When a compound such as 2-chloroanthraquinone is being aminated, solution is facilitated by increasing either the NH_3 concentration or the temperature. Both of these factors incidentally increase the partial pressure or activity of the dissolved ammonia.

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[1] PINCK and HETHERINGTON, *loc. cit.*

[2] SCHOLL and DAVIS, *Ind. Eng. Chem.*, **29**, 202 (1937).

[3] U. S. 2,164,706 (1939); U. S. 2,191,361 (1940); U. S. 2,287,597 (1942).

[4] U. S. 2,301,629 (1942); U. S. 2,373,869 (1945).

From Fig. 8, showing the vapor pressure (extrapolated) of ammoniacal solutions at various molalities, it can be seen that an ammonia partial pressure of 800 lb. per sq. in. can be obtained at 200°C. with a 30 molal solution, at 165°C. with a 40 molal solution, and at 140°C. with a 50 molal solution. Experience in the ammonolysis of halogenoanthraquinones has shown that lower temperatures suffice when the NH_3 concentrations are increased. The permissible diminution in operating temperature is not, however, so great as one would expect from the vapor-pressure curves.

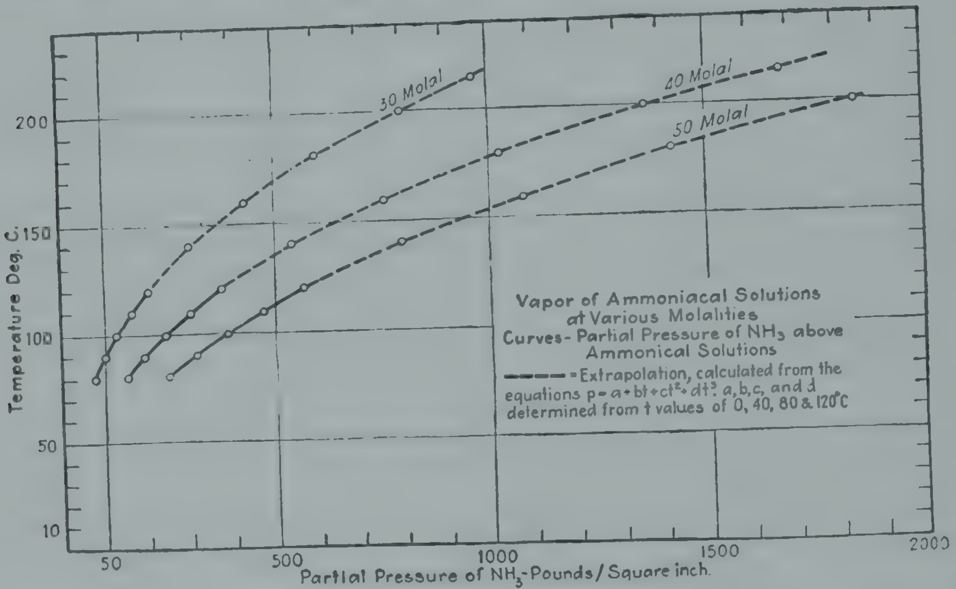

Fig. 8.—Extrapolation NH_3 vapor pressure.

When more dilute NH_3 solutions are employed, the results obviously suffer from the increased activity of the solvent—water. Experience in the preparation of aniline, *p*-nitroaniline, aminoanthraquinones, and ethylenediamine from the corresponding halogeno compounds demonstrates that the yields and purity of primary amine are invariably favored by the utilization of the highest practical concentrations of ammonia.

Effect of Agitation.—In liquid-phase ammonolysis, the rate of amination depends upon the homogeneity of the reaction mass. Without agitation, some insoluble compounds would, on account of their greater density, settle to the bottom of the autoclave while the ammonia liquor remained as a distinct layer above it. Reaction would then take place only at the interface, and a complete conversion of the compound to the amino derivative would not be feasible.

Such a problem exists in the ammonolysis of 2-chloroanthraquinone.

In this instance, the solid aromatic compound does not wet out and has a tendency to remain on the surface of the ammoniacal solution. Since this amination apparently takes place in the liquid phase, it is impossible to obtain satisfactory results in this operation unless the type of agitation provides a practically homogeneous reaction mass.

In some operations, where no stirrers are provided, the mixing of the reacting materials depends on the convection currents produced by a flame at the base of the autoclave or on forced circulation through a tubular system. The influence of speed of stirring on the reaction velocity of a number of unit processes has been worked out by Huber and Reid, who found that three classes existed:[1]

> . . . (1) those in which the rate of reaction is a linear function of the speed of stirring; (2) those in which this relation becomes linear only after a certain speed is attained, it being very slow without stirring, the rate increasing at first far more rapidly than the speed of stirring; and (3) those in which the rate is independent of the speed of stirring.

Ammonolysis of sparsely soluble substances in aqueous ammonia is largely included in the second class—without agitation practically no reaction taking place. A slight stirring brings about a substantial increase in the reaction velocity, but a proportionate increase in the rate of reaction is not produced by a more vigorous agitation.

When soluble substances such as chloroacetic acid and 4′-chloro-2-benzoylbenzoic acid are aminated, the problem of agitation ceases to be of major importance.

Wetting Agents.—In the amination process, the problems of solubility and agitation are closely associated with reaction rates, for it is clear that the reacting molecules must be brought together. Mention has already been made of the difficulty in obtaining a practically homogeneous reaction mass when treating compounds of meager solubility such as chloroanthraquinone and *p*-nitrochlorobenzene with aqueous ammonia. Although it is known that a more concentrated ammonia is a superior solvent and permits more rapid aminations, little is known regarding adsorption of organic compounds on the surface of aqueous ammonia of various concentrations.

There is also a dearth of information regarding the efficacy of emulsifying and wetting agents in the amination process. Such agents appear to have important potential utility in the ammonolysis of aryl halides such as chlorobenzene and chloroanthroquinone which have only limited solubility and which, on ammonolysis, yield weak bases that do not form stable hydrochlorides under operating conditions. With compounds of this class, it would be expected that a surface-active agent such as soap would (1) wet and emulsify the reactants and thus hasten the reaction; (2) act as a buffer for hydrogen ions, by the formation of sodium chloride and free fatty acid; and (3) provide a protective film for the autoclave surface, thus inhibiting corrosion and contributing to the production of a purer solid amine. The residual ammonium soap would have to be removed by appropriate means in subsequent operations.

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[1] Huber and Reid, *Ind. Eng. Chem.*, **18**, 535 (1926).

The accelerating influence of soap on the speed of reaction in aminating ethylene dichloride is evidenced by the curves in Fig. 9.[1]

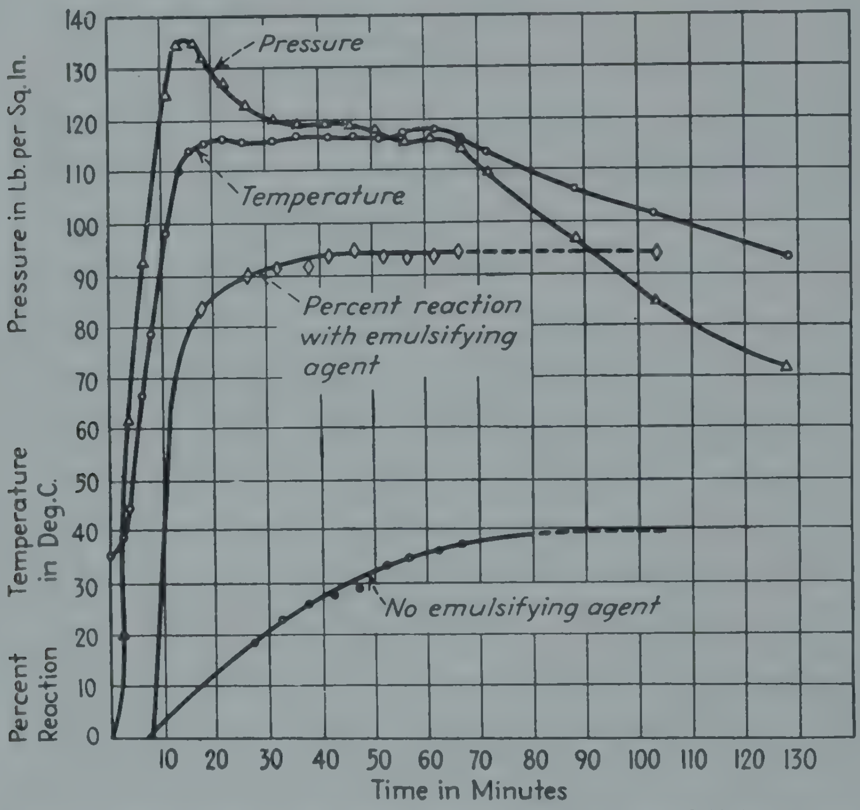

Fig. 9.—Amination of ethylene dichloride; effect of emulsifying agent.

Effect of Halogen Derivative.—From the known activity of the halogens and the heats of formation of the halides, it would be expected that replacement of bromine atoms could be accomplished more readily than that of chlorine atoms. This has been found to be true in the treatment of the respective halogenoanthraquinones. Thus, without the employment of catalysts, bromoanthraquinone is approximately twice as reactive as the chloro derivative. When a copper catalyst is used, 2-aminoanthraquinone of 97 to 98 per cent purity can be obtained with a 28.5 per cent NH_3 solution, whereas the maximum purity of product from the chloro derivative under the same conditions is only 93 per cent.

[1] Barbieri, U. S. 2,078,555 (1937); Barbieri and Heard, U. S. 2,113,640 (1938).

The comparative ease in replacing —Br by —NH_2 is brought out in the conversion of 4-bromochlorobenzene to 4-chloroaniline. By heating with aqueous ammonia at 120°C. for 10 hr., only the bromine atom is replaced by the amino group.[1]

Effect of Nitro Substituents.—The conversion of chlorobenzene to aniline requires a comparatively high temperature—200°C. or above—and the presence of a catalyst. When certain negative groups such as the —NO_2 or —COOH are introduced in the phenyl nucleus, the replacement of the halogen atom takes place more readily. Thus, it is a comparatively easy procedure to produce the nitroanilines from the corresponding halogeno-nitrobenzenes. No catalyst is required in this operation, and a temperature of 170°C. suffices.

The labilizing influence of the nitro group is demonstrated by the work of McMaster and Steiner in the amination of nitro-*p*-dichlorobenzene.[2] Whereas *p*-dichlorobenzene cannot readily be aminated, the introduction of the nitro group makes possible the replacement of the ortho halogen at 150°C. without the assistance of a catalyst.

Sprung, in studying the reactivities of the chloro- and bromonitrobenzenes with alcoholic sodium sulfite to form nitrobenzenesulfonates, also found that the introduction of more than one nitro group greatly increases the activity of the halogen atom.[3]

The ease in replacing halogen in halogenonitrobenzenes is, in all probability, due to the activity of the nitro group in forming addition complexes. Garner and Gillbe have shown that dinitrobenzene forms addition complexes with ammonia that show measurable conductivities.[4] It is logical to assume that the point of contact is the oxygen of the nitro group. Here each oxygen has only two of its six available electrons saturated as bond energy, and the remaining atomic energy is available in part for auxiliary attachments.

Energy Factors in Ammonolysis. *Effect of Temperature.*—The generally accepted explanation for the temperature coefficient of reactions is essentially the Arrhenius hypothesis of activated molecules. Tolman has elaborated this principle in a comprehensive manner on the assumption that there is a whole series of active molecules in statistical equilibrium with the inactive ones and that the active molecules differ from the inactive only in their energy content; each of these active molecules has a finite probability of reacting, which depends upon this energy content.[5] On this hypothesis, the energy of activation is the difference

[1] Mills, U. S. 1,935,515 (1933).

[2] McMaster and Steiner, *Ind. Eng. Chem.*, **22**, 547 (1930).

[3] Sprung, *J. Am. Chem. Soc.*, **52**, 1650 (1930).

[4] Garner and Gillbe, *J. Chem. Soc.*, 2889, (1928).

[5] Tolman, *J. Am. Chem. Soc.*, **47**, 2652 (1925).

of the mean energy of the molecules that react and the mean energy of all the molecules.

An increase in the temperature of amination increases not only the solubility and internal energy of the compound that is being treated but also the partial pressure of the ammonia. Since the activity of the aqueous ammonia is a function of the total and NH_3 partial pressures, the probabilities of reacting are increased in proportion to the temperature. The partial pressure of H_2O in NH_3 *aq.* increases at a greater rate with increasing temperature, causing hydrolysis to occur to a greater extent. This is illustrated by the data in Table VII, relating to the noncatalytic preparation of *p*-nitroaniline.

Effect of NH_3 Concentration.—It is necessary to distinguish between the terms *ammonia ratio* and *ammonia concentration*. The first relates to the capacity factor of the system; the second, to the intensity factor. Aside from economic considerations, there are no disadvantages in using a large ratio of aqueous ammonia (25 to 35 per cent NH_3 solution) with respect to the compound being treated. Within reasonable limits, an increase in this ratio promotes both the yield and purity of primary amine obtained. The larger volume of concentrated aqueous ammonia promotes solubility and therefore causes the reaction to take place more readily.

TABLE VII.—NONCATALYTIC AMMONOLYSIS OF *p*-CHLORONITROBENZENE[1]
Influence of NH_3 Concentration, NH_3 Ratio, and Temp.

Expt. no.	Temp., °C.	Time, hr.	NH_3 conc., %	$ClC_6H_4NO_2$, mole	Cl^-, %	*p*-Nitroaniline, %	Mole ratio, $NH_3/ClC_6H_4NO_2$
1	140	4	21	0.4	1.63	1.31	9.375
2	140	4	35	0.4	3.52	3.09	9.375
3	140	4	21	0.1	4.71	3.64	37.5
4	140	4	35	0.1	6.81	6.26	37.5
5	180	4	21	0.1	82.73	78.67	37.5
6	180	4	35	0.1	91.88	89.16	37.5
7	200	4	21	0.1	97.71	93.47	37.5
8	200	4	35	0.1	98.80	95.56	37.5
9	200	1	21	0.025	36.19	31.74	150.0
10	200	1	28	0.025	36.81	33.98	150.0
11	200	1	35	0.025	36.80	35.68	150.0
12	200	1	21	0.025	36.19	31.74	150.0
13	200	1	28	0.025	35.36	32.82	200.0
14	200	1	35	0.025	30.12	28.26	240.0

[1] See technical section for description of industrial procedure. Molar NH_3 ratios in excess of 37.5 are impractical.

Extensive investigations in the ammonolysis of halogeno compounds have shown that the practical advantages to be obtained by utilizing a more concentrated NH_3 solution for noncatalytic aminations may be summed up as follows: (1) Amination is more rapid; (2) conversion of reacting compound to primary amine is more complete; (3) formation of secondary and tertiary amines and hydroxy compounds is inhibited; (4) lower reaction temperatures can be used; and (5) since larger batches can be treated with the same quantity of liquor, economies in the number of pieces of equipment can be effected. To a large extent, these observations are confirmed by the data in Table VII relating to the preparation of *p*-nitroaniline and the curves of Fig. 10 relating to xenylamine.

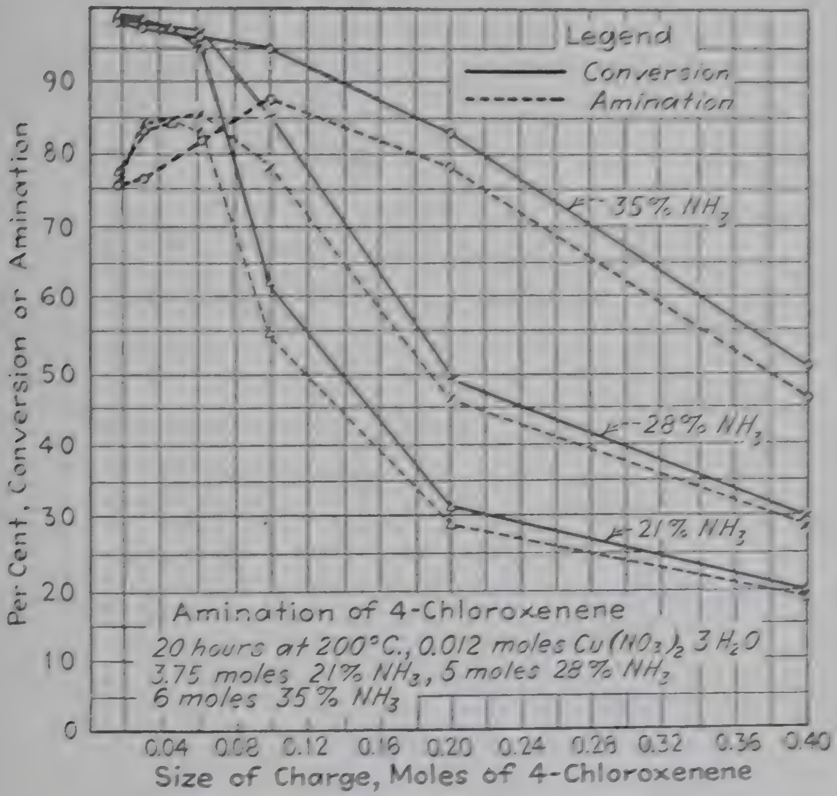

FIG. 10.—Amination of 4-chloroxenene.

The effect of NH_3 concentration in catalytic ammonolysis has been investigated by Vorozhtzov and Kobelev and by Groggins and Stirton.[1,2] The practical benefits of employing higher ammonia concentrations are brought out clearly by the data in Table VIII. In these experiments, as in plant practice, a constant ratio of ammonia and copper to 4-chloroxenene was provided. From the tabulated data, it can be concluded: (1) for any particular NH_3 concentration, within limits, the rate of conversion is a function of the copper-ammonia concentration; (2) most of the

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[1] VOROZHTZOV and KOBELEV, *J. Chem. Soc.* (*U.S.S.R.*), **4**, 310 (1934).

[2] GROGGINS and STIRTON, *Ind. Eng. Chem.*, **28**, 1051 (1936).

generalizations relating to the noncatalytic ammonolysis of halogeno compounds are equally valid; (3) the difference between conversion, *i.e.*, decomposition of halogeno compound as determined by chloride ion, and amination, for 18 per cent copper, is approximately twice as great as that for 12 per cent copper; and (4) as the ammonia concentration is increased, this "difference" becomes less despite the fact that the reaction has proceeded farther.

Table VIII.—Influence of Ammonia Concentration in Preparation of Xenylamine
16 Hr. at 200°C.

Expt. no.	NH_3 conc., %	Aqueous NH_3, gm.	4-Chloroxenene, mole	$Cu(NO_3)_2 \cdot 3H_2O$, mole	Catalyst conc., gr. atom copper per liter	Conversion, A, %	Amination B, %	100 × mole ratio, Cu : R·Cl	Mole ratio NH_3 : R·Cl	Difference, A − B
1	14	304	⅙	0.03	0.0932	55.31	45.14	18	15	10.17
2	21	304	¼	0.045	0.1360	66.20	57.68	18	15	8.52
3	28	304	⅓	0.06	0.1770	86.35	80.15	18	15	6.20
4	35	292	⅖	0.072	0.2169	93.26	88.77	18	15	4.49
5	21	304	¼	0.072	0.2175	85.56	73.82	28.8	15	11.74
6	14	304	⅙	0.02	0.0621	41.20	35.73	12	15	5.47
7	21	304	¼	0.03	0.0906	58.38	53.44	12	15	4.94
8	28	304	⅓	0.04	0.1180	74.10	71.35	12	15	2.75
9	35	292	⅖	0.048	0.1446	87.02	84.41	12	15	2.61
10	35	292	¼	0.048	0.1446	98.92	88.99	19.2	24	9.93
11	21	304	¼	0.048	0.1450	73.38	64.06	19.2	15	9.32

According to Groggins and Stirton.

Reaction-rate studies with aryl chlorides showed that the effect of NH_3 concentration on the rate of conversion in catalytic ammonolysis depends upon (1) the ammonia ratio; (2) the reaction temperature; and (3) the halogeno compound.[1]

Effect of Free Space in Autoclaves.—Associated with the factor of NH_3 concentration is the influence of *freeboard*, or the free space in the autoclave. This is a matter of importance which must be taken into careful consideration in carrying out operations involving ammonolysis. It is obviously advantageous to fill the autoclave up to its maximum safe capacity. Such conditions permit a larger production and generally give a better yield and purity of product. When aminations involving insoluble halides such as halogenoanthraquinones are carried out in glass tubes, it will be observed that the reaction takes place in the liquid phase. The solid material remaining above the surface of the liquid does not appear to react, despite the fact that it is in contact with vapors that are essentially gaseous ammonia.

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[1] Groggins and Stirton, *Ind. Eng. Chem.*, **28**, 1051 (1936).

When an excess of freeboard is left in the autoclaves, this space will be filled with vapors in equilibrium with the aqueous solution. The greater the free space the greater will be the quantity of ammonia that goes from the liquid to the vapor phase, thus actually lowering the active NH_3 ratio and concentration. Since ammonolysis of sulfonic acid and halogeno compounds takes place in the liquid phase, it is obvious that the best results can be obtained only by introducing the maximum-size charge into the autoclave, with due consideration to the increased temperature coefficient of expansion of more concentrated aqueous ammonia.

V. METAL CATALYSTS IN AMMONOLYSIS OF HALOGENO COMPOUNDS

Compounds of metals following hydrogen in the electrochemical series; *e.g.*, arsenic, copper, and silver, can advantageously be employed in the conversion of certain halogeno compounds to amino derivatives.[1] Their efficacy in a number of aminations has been somewhat exaggerated in the patent literature, where apparently many of the claims are inserted merely for protective purposes. This is particularly true in the amination of aromatic compounds containing a nitro group. Thus, in the conversion of *p*-nitrochlorobenzene to *p*-nitroaniline, it has been found that the use of copper and its salts, although permitting lower reaction temperatures, gives rise to an inferior product—probably on account of the formation of copper salts of enolized nitroaniline. McMaster and Steiner failed to find any advantages in the use of copper in the preparation of *p*-chloro-*o*-nitroaniline from nitro-*p*-dichlorobenzene; and Grether and Keener used no catalyst in the ammonolysis of 1, 2-dichloro-4-nitrobenzene.[2,3]

Copper and Its Salts as Catalysts.—From studies on aniline, it has been presumed that cuprous salts alone are satisfactory whereas cupric salts are practically ineffective. Such general conclusions are, however, not justified. It is probable that certain practical factors; *i.e.*, susceptibility of amine to oxidation, inherent in the ammonolysis of chlorobenzene make the presence of metallic copper, along with a cuprous salt, desirable. The fact that cupric nitrate serves as well as cuprous salts in the ammonolysis of chloroxenene, chloronaphthalene, and chloroanthraquinones indicates that no generalization can be made with respect to the advantages of univalent copper.

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[1] Groggins, Stirton, and Newton, *Ind. Eng. Chem.*, **23**, 893 (1931).

[2] McMaster and Steiner, *loc. cit.*

[3] Grether and Keener, U. S. 1,882,811 (1932).

The anion accompanying the copper is not without influence, since the introduction of hydroxyl or nitrate ions also affects the known reactions. The more favorable action of cuprous salts in the preparation of aniline and *p*-phenylenediamine may be explained by assuming that these amines are readily susceptible to catalytic oxidation by the anion of the cupric salt. The concentration of copper for the conversion of chlorobenzene is, consequently, reduced because some of it enters into the second catalytic reactions, *viz.*, the oxidation of aniline. In support of the oxidation theory, it is known that (1) cupric and cuprous compounds are about equally active in the preparation of amines that are not readily susceptible to oxidation; (2) in the preparation of easily oxidizable amines, low catalyst concentration results in a smaller difference in the reaction rates when cuprous and cupric compounds are compared; and (3) the treatment of aniline with cupric nitrate leads to a much greater oxidation of amine than with cuprous chloride.[1] The preceding observations explain why cupric compounds and oxidants may be used to advantage in the preparation of aminoanthraquinone and must be avoided in the preparation of aniline. In those aminations which require copper, copper ammonia cations seem to serve as cyclic catalysts comprising halogeno compound, ammonia and copper, which subsequently undergo metamorphasis during the course of the reaction.

The action of aqueous ammonia on copper, particularly in the presence of ammonium salts, indicates quite clearly that the pressure system could not be constructed from this metal.

VI. CORROSION AND THE pH OF THE AUTOCLAVE CHARGE

Groggins and Stirton showed that the pH of aqueous ammonia decreases with rising temperature and more rapidly under such conditions when ammonium salts are introduced.[2] During the course of the reaction in the liquid-phase treatment of halogeno compounds, the concentration of NH_3 in the charge diminishes while that of the hydrohalide increases. It is important to remember that during ammonolysis, the molar concentration of the hydracid must be *at least* equivalent to the molar concentration of the amino compound, because of the concomitant formation of hydroxy compounds and secondary and polyamines. The hydrohalide may be distributed as free acid, as ammonium halide in solution, and as the salt of the newly formed amino compound. These are all acidic compounds (proton donors); and unless their activity is neutralized, they will corrode steel vessels. The pH of the molar solutions of such compounds at 25°C. is closely as follows: NH_4Cl, 4.7; $CH_3NH_2\cdot HCl$, 5.5; $C_2H_5NH_2\cdot HCl$, 6.0; $C_6H_5NH_2\cdot HCl$, 2.3.

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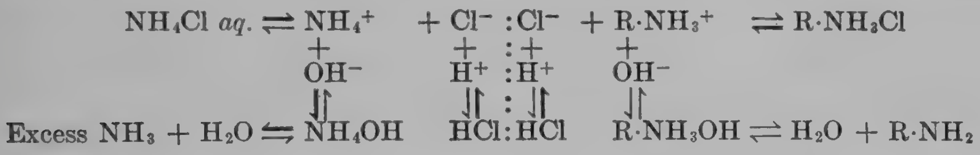
[1] Groggins, *Ind. Eng. Chem.*, **28**, 1051 (1936).

[2] Groggins and Stirton, *Ind. Eng. Chem.*, **25**, 42 (1933).

In closed systems containing an excess of aqueous ammonia in addition to corresponding molal concentrations of hydrochloric acid and primary amine, the equilibriums involved may be represented as follows:



$$\begin{array}{rccccccl} \text{NH}_4\text{Cl } aq. \rightleftharpoons & NH_4^+ & + Cl^- & : & Cl^- & + R\cdot NH_3^+ & \rightleftharpoons R\cdot NH_3Cl \\ & + & + & : & + & + & \\ & OH^- & H^+ & : & H^+ & OH^- & \\ & \downarrow\uparrow & \downarrow\uparrow & : & \downarrow\uparrow & \downarrow\uparrow & \\ \text{Excess } NH_3 + H_2O \leftrightharpoons & NH_4OH & HCl & : & HCl & R\cdot NH_3OH & \rightleftharpoons H_2O + R\cdot NH_2 \end{array}$$

The available information regarding these reactions at high temperatures is inadequate, and our knowledge relates only to certain segments of the whole. There is little doubt, however, that the principal factors affecting the equilibriums are (1) the temperature of the system; (2) the relative basicity of the amine; and (3) the solubility of the amine.

Because of its volatility, NH_3 can be displaced from $(H(NH_3))Cl$ by basic substances of higher boiling point. The rate at which such displacement occurs, however, obviously depends on the strength of the base, *e.g.*, $Ca(OH)_2$, Alk.NH_2, etc., the reaction temperature, and the counter influence of free NH_3. It is known, however, that with increasing temperature, NH_3 has a diminishing capacity to form the ionogen NH_4OH; and at 290°C., the union of NH_3 to HCl in aqueous $(H(NH_3))Cl$ is so weak that the two components react as if they were alone, and ammonium chloride in aqueous solution can be employed to convert methanol to dimethylamine[1] and *sym*-xylenol to dixylylamine. The fact that the charge and free space in the autoclave contain a large excess of gaseous ammonia does not, therefore, signify that the hot aqueous ammonia has the capacity to displace the amine from all amino hydrohalides, for there is ample evidence to the contrary. When the amino hydrohalide is insoluble, then the concentration of the $R\cdot\overset{+}{N}H_3$ ions in solution is diminished. In general, it can be concluded that the slightly basic arylamines do not form stable hydrohalides at the high temperatures necessary for conversion but the highly basic alkyl and alkanolamines do form stable salts of limited solubility.

From the extensive literature on inhibitors, it would be expected that the amino compound being synthesized should serve as its own inhibitor, and indeed it would form a protective film if sufficient free base were available. It is well known that the addition of aniline to aniline hydrochloride will reduce the dissociation and, consequently, the corrosive action of the latter. This probably explains why it has been found efficacious to add acid inhibitors, *e.g.*, alkylamines, secondary amines, and pyridine, to the autoclave charge in the preparation of nitroamines,[1] for this procedure ensures the presence of free base during ammonolysis.

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[1] Bottoms, U. S. 2,085,785 (1937).

There are two other useful methods of controlling the pH of the autoclave charge; *viz.*, the introduction of copper-ammonio hydroxides[2] and the use of buffer salts,[3] such as soap or chlorates, which are attacked and decomposed when the concentration of the hydracid is sufficiently great. The oxidants cannot be used to advantage, however, when the amino compound, *e.g.*, aniline, is readily susceptible to oxidation.

VII. EQUILIBRIUM CONSIDERATIONS IN AMMONOLYSIS

The data in Table IX[3] pertaining to the amination of 2-chloroanthraquinone are of interest not only because the controls show results that compare favorably with those obtained by the use of copper but particularly because the experiments at 190 to 200°C. show only a maximum divergence of 0.35 per cent from the mean purity of 91.25. It appears, therefore, that despite a high NH_3 ratio, a purity of about 91.5 represents the best results obtainable under such operating conditions. It is necessary, therefore, to conclude that, owing to the concentration of arylammonium chloride, an equilibrium is established that at lower temperatures (180 to 190°C.) prevents complete conversion and at higher temperatures (205 to 220°C.) serves only to introduce impurities in the reaction product.[4]

TABLE IX.—CONTROLS. AMMONOLYSIS OF 2-CHLOROANTHRAQUINONE
28 Per Cent NH_3 *Aq.*, 315 Gm. Capacity of Autoclave, 500 Cc. Mean Purity, Expts. 2 to 6, Incl., 91.25 Per Cent

Expt. No.	2-Chloroanthraquinone, gm.	Temp., °C.	Time, hr.	Yield, %	Purity, %
1	36.375	180	30	98.4	80.8
2	36.375	188	30	97.4	88.7
3	36.375	190	30	98.0	91.1
4	36.375	195	24	94.5	91.4
5	36.375	200	18	95.5	91.0
6	42.5	195	24	95.6	90.9
7	42.5	200	30	94.6	91.6
8*	42.5	195	24	96.0	88.5

* Containing 0.05 gm. CuO and 0.25 gm Cu.

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[1] Dahlen and Foohey, U. S. 2,072,618 (1937).

[2] Britton and Williams, U. S. 1,726,170 (1929).

[3] GROGGINS and STIRTON, *Ind. Eng. Chem.*, **25**, 169 (1933).

[4] See GROGGINS and NEWTON, *Ind. Eng. Chem.*, **21**, 369 (1929), for aminations at 215 to 220°C.

By analogy with esterification, it would appear logical that the reaction could be favorably completed by removing one of the products of reaction, *viz.*, ammonium chloride. It is not surprising, therefore, that compounds introducing hydroxyl ions may be employed advantageously, especially in the preparation of easily oxidizable amines from R-Cl compounds, but a compensatory penalty in the form of hydroxy impurities is to be expected.

Effect of Inorganic Oxidants on Equilibrium.—In the preparation of amines that are not readily oxidized, *e.g.*, aminoanthraquinones, oxidation has been found to be a satisfactory method of counteracting the influence of hydrochloric acid or its ammonium salts. The use of oxyhalogen compounds, particularly chlorates, leads to consistently improved results. The efficacy of potassium chlorate may possibly be accounted for by the following reaction:[1]

$$6R{\cdot}N\overset{+}{H}_3\,Cl^- + KClO_3 \rightarrow 6R{\cdot}NH_2 + KCl + 3H_2O + 3Cl_2$$

The chlorate serves, apparently, as a buffer to control the hydrogen- or ammonium-ion concentration.[2] The fate of the chlorine in the suggested mechanism of reaction is not definitely known. It may (1) directly or indirectly oxidize the iron surfaces of the autoclave and (2) oxidize some of the amine, evidence of which is generally obtainable and frequently apparent.[3]

VIII. SPECULATION REGARDING MECHANISM OF THE REACTION

The mechanism of ammonolysis appears to be identical with the usual process involving replacement in the benzene series, whose initiation is determined by the presence of key atoms such as Cl, N, C═C, and O.[4] The necessary conditions are chemical unsaturation or the presence of electrons capable of forming covalent bonds resulting in the formation of addition compounds that undergo ionization. This is followed by a rearrangement to a compound with principal valences. The final stage is stabilization, which is best interpreted as an intramolecular ionic effect. In the Friedel and Crafts reaction, this is accompanied by a splitting off of HCl; in nitration, there is a splitting off of bound nitric or other acid anion with the loosened hydrogen of the neighboring carbon atom; and in ammonolysis, there is a splitting off of the hydrogen or ammonium compound of the negative atom or radical that has been replaced:

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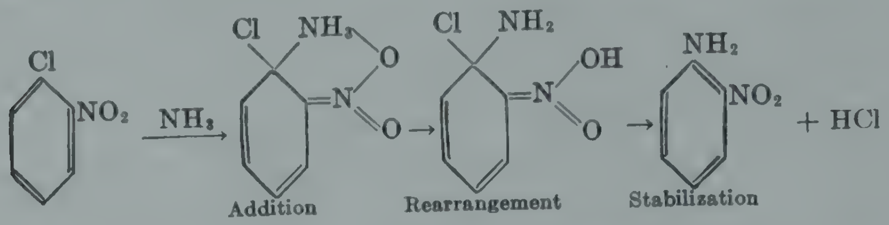
[1] Groggins and Stirton, *Ind. Eng. Chem.*, **25**, 171 (1933).

[2] Mono- and dinitrobenzenoid compounds are likewise preferentially reduced but, unlike oxyhalogen compounds, introduce undesirable reaction products, either with the amino compound or with the aqueous ammonia. Lead peroxide and lead tetracetate may also be used.

[3] Groggins and Stirton, *Ind. Eng. Chem.*, **28**, 1051 (1936).

[4] Wohl and Wertyporoch, *Ber.*, **64**, 1308 (1931).



In noncatalytic aminations, it is assumed that the first stage is the formation of an addition complex between ammonia and the organic compound. In the presence of an excess of ammonia, this is probably a reaction of the first order, and the limiting factor in the formation of the complex is the solubility of the compound to be aminated. It is presumed that during the intramolecular rearrangement from the addition complex to the stable compound, there is a shift from a covalent to an electrovalent bond. The following formulations show how such solute-solvent complexes resemble the more stable addition compounds of the amines:

$$\text{R}\cdot\text{Cl} + \text{NH}_3 \rightarrow \text{R(NH}_3\text{)Cl} \rightarrow \text{R}\cdot\text{N}\overset{+}{\text{H}}_3\cdot\overset{-}{\text{Cl}}$$

$$\text{R}\cdot\text{OH} + \text{NH}_3 \rightarrow \text{R(NH}_3\text{)OH} \rightarrow \text{R}\cdot\text{N}\overset{+}{\text{H}}_3\cdot\text{O}\overset{-}{\text{H}}$$

$$\text{R}\cdot\text{SO}_3\text{H} + \text{NH}_3 \rightarrow \text{R(NH}_3\text{)SO}_3\text{H}^{*} \rightarrow \text{R}\cdot\text{N}\overset{+}{\text{H}}_3\text{OSO}_2\overset{-}{\text{H}}$$

* The ammonium salt is undoubtedly first formed.

The concentration of such salts or bases determines the equilibrium of the reaction for each temperature. When the ammonia system is cooled, the power of NH_3 to form the ionogen NH_4OH increases, and the distribution of the hydracid (in the ammonolysis of halogens) would depend on the basicity of the amino compound and the solubility of its salts.

Previously, it was shown that in the ammonolysis of carbonyl compounds, an aldol type addition reaction occurred with the formation of a secondary alcohol, the elements of water being eliminated by conjoint reduction. In the vapor-phase ammonolysis of alcohols, addition may occur with the formation of the ammonium alcoholate, which, in the presence of a dehydrating agent, decomposes into amine and water. The initial dehydration of the alcohol to an olefin that adds $H—NH_2$ is also possible.

IX. DESIGN AND CONSTRUCTION OF EQUIPMENT

The preparation of amines through the reaction between organic compounds and ammonia generally takes place at elevated temperatures and pressures. It is, therefore, essential that the ammonolysis be carried out either in high-pressure autoclaves or in tubular systems. Autoclaves are generally adapted for discontinuous or batch operations, whereas tubular systems are particularly suitable for continuous high-pressure syntheses.

Direct-fired Autoclaves.—The use of direct-fired autoclaves for carrying out high-pressure reactions was at one time a general practice. Coke, fuel oil, and gas furnished the means of heating such vessels. To a large extent, however, the firebox has been replaced by the jacket for steam or circulated fluid heat-transfer agents. Such installations provide a safer, more accurate, and automatic control of the reaction.

In a limited number of operations, direct-fired operations are still used, principally on account of the fact that heating by such means sets up convection currents in the charge and thus obviates the necessity of using mechanical stirrers. In the vapor-phase ammonolysis of alcohols and aldehydes wherein the reactants pass through heated tubes containing a catalyst, direct fire or electric heat can be used to advantage.

The autoclave is provided with nozzles for charging and discharging connections and with a thermometer well. The head is a massive steel forging that seals the vessel by means of a carefully machined tongue-and-groove joint. The head is made fast with chrome-steel bolts and is removed only when the autoclave is given a thorough periodical inspection. A heavy-walled seamless steel tube is frequently threaded and welded to the head. To this tube, connections are made for the safety valve and frangible disk, pressure gauge, and vent lines.

Ammonolysis in Jacketed Vessels.—When the operating temperature is sufficiently low, *i.e.*, 190°C. or lower, steam is generally employed in jacketed vessels. Above 190°C., it is customary to employ an oil circulating system or to heat with hot water under pressure. The advantages of jacket equipment over nonregulated, direct-fired apparatus may be set down as follows: (1) automatic control; (2) fuel economy; (3) saving of labor; (4) uniform temperature and product; (5) greater productivity per machine on account of the ease in cooling; and (6) better yields and purer product. Most of these advantages can be obtained by induction heating or in gas- or oil-fired systems that are equipped for automatic control.

The inner vessel of the jacketed autoclave is similar to that used for direct fire. A steel shell designed to withstand the jacket pressures is welded to the outside, and the autoclave is then suspended on a suitable steel structure. When steam is used for heating, it is delivered to the upper portion of the jacket, and the condensate is drained by trap connections at the base. Because heating with steam or oil creates a uniform temperature throughout the charge, it is necessary to provide mechanical agitation for charges that are not homogeneous. In the ammonolysis of aromatic halides, such as *p*-nitrochlorobenzene, the denser molten aromatic compound would, in the absence of mechanical agitation, settle out at the base with the lighter aqueous ammonia above it. Conversion to amine would then take place only at the interface of the two layers.

In the ammonolysis of compounds that are difficult to wet out and that are converted only at high temperatures, it is advisable to employ horizontal autoclaves. Such systems provide the necessary freeboard with a much smaller distance between the charge level and the top of the vessel. Horizontal vessels of this kind are provided with a number of rotating splash arms which wash any suspended material from the top of the autoclave. Such a vessel is particularly suitable for the conversion of 2-chloroanthraquinone. In vertical pressure vessels, it is therefore necessary to use a sleeve-and-turbine agitator, which drags the 2-chloroanthraquinone down into the aqueous ammonia.

Heat Conservation.—Amination reactions are *exothermic*, and the jackets of jacketed autoclaves need to be well insulated. About 8 to 12 in. of insulation is desirable, and its use is amply rewarded by (1) better operating conditions, which is important when working with amino compounds; (2) a marked saving in fuel consumption; and (3) the ability to carry out aminations at temperatures above that of the available steam. The exothermic reaction in well-insulated autoclaves causes a rise of 15 to 30°C. in temperature after the jacket steam has been cut off.

Tubular Pressure Systems.—A tubular or pipe pressure system is sometimes used to carry out the amination. The seamless steel tubing used for such construction is capable of withstanding pressures up to 1,000 atmos. Such a system is particularly useful where exceptionally high pressures are encountered or where continuous operations are practicable. A further advantage resides in the fact that the pressure coils comprising the reaction system contain only a relatively small quantity of material in process. Such a system may be subdivided into a number of units, each immersed in an oil or metal bath controlled at the desired temperature. Pressure gauges and safety diaphragms are placed on each unit of the system to ensure safe operations.

Auxiliary High-pressure Equipment.—The design and selection of proper auxiliary equipment for high-pressure reactions are as essential as choosing the pressure equipment itself. The successful operation of the whole system depends on the proper functioning of such accessories.

In well-organized plants, thermoelectric equipment is employed to regulate the temperature. Experience has shown that such devices can be relied upon to give satisfactory service.

Asbestos and lead gaskets have been found most satisfactory for sealing flanged connections in the pressure system. The metal gasket is usually employed for joints that are opened only infrequently.

Discharge lines from the autoclaves are customarily equipped with two heavy-duty steel valves, one of which is a globe or cone valve and the other a gate valve. The former is placed adjacent to the autoclave to hold the pressure and is supplied with cut asbestos gaskets, which are renewed for each run. The gate valve has many important uses in technical operations, the most obvious being the feasibility of cutting out individual autoclaves from the rest of the system.

In plant operations, it is not advisable to depend on safety or relief valves to release extraordinary pressures. It has been found best to employ a metal diaphragm supported between two steel flanges, these fittings being part of a pipe line leading directly from the autoclave. Such frangible disks should be tested accurately under precise conditions to vouchsafe rupture at definite pressures. Tin and nickel sheets have proved satisfactory for autoclaves containing ammonia. It is desirable to protect the face of the diaphragm next to the reaction vapors with a thin sheet of asbestos. Some engineers approve of placing after the diaphragm a pop valve, which will reseat after the excessive pressure has been dissipated. This valve is always set to blow about 50 lb. below the bursting point of the frangible disk. Thus, a rupture in the diaphragm is sure to be followed by the opening of the relief valve, which has been completely protected from the corrosive vapors of the autoclave. With an arrangement of this character, it is usually feasible to complete the run and then replace the metal disk and overhaul the pop valve. The possibility of effecting material savings by such arrangement is obvious.

X. TECHNICAL MANUFACTURE OF AMINO COMPOUNDS

Ethylenediamine from Ethylene Dichloride.—The preparation of ethylenediamine from the dichloro compound is described by Curme as follows:[1]

The reaction vessel 1 (Fig. 11) is charged initially with the quantity of ammonia that will provide the desired NH_3 ratio, and this ammonia circulates through a cycle comprising the lines 6 and 9 and the tower 7. Ammonia is thereafter introduced into vessel 1 in such quantity as is sufficient only to replace that which is removed from the system as its derivative ethylenediamine, in combination as ammonium chloride if the latter is not decomposed in the apparatus, through leakage, or as free ammonia not recovered from the diamine solution.

The contents of the reaction vessel are kept in agitation, and a temperature sufficient to cause the reaction to proceed at a suitable rate—110 to 150°C.—is maintained.

The overflow through line 6 consists of an aqueous solution of ethylenediamine hydrochloride, ammonium chloride, and ammonia. As it passes down through tower 7, this liquid is gradually heated above the

[1] Curme, U. S. 1,832,534 (1931).

temperature prevailing in the reaction vessel, and the ammonia is expelled as in standard ammonia-distillation practice. This ammonia is returned through line 9 to the reaction vessel 1 so that the requisite excess of ammonia is maintained in the reaction vessel.

It will be noted that a part of the ammonia added leaves the vessel 1 as ethylenediamine hydrochloride. This may be decomposed for the recovery of its ammonia, either in a separate apparatus or in the same apparatus in which the free ammonia is recovered. In the drawing is shown a storage tank from which a strong base, such as sodium hydroxide, may be continuously fed into the column 7 in quantity sufficient to liberate the combined ammonia. Enough base may be used if desired to decompose the ethylenediamine hydrochloride and liberate the diamine, which, like the hydrochloride, is soluble in water.

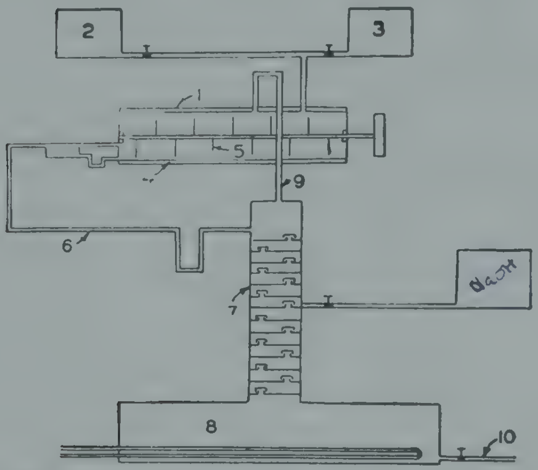


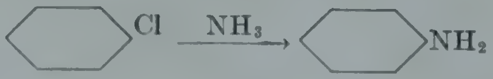
Fig. 11.—Reaction system; preparation of ethylenediamine.

1. Pressure reactor.
2, 3. Holders for ammonia liquor and ethylene dichloride.
4. Heating jacket.
5. Stirrer.
6. Overflow line.
7. Ammonia vaporizing column.
8. Kettle with heating coil.
9. Ammonia return line to reactor.
10. Discharge line for ethylenediamine.

The ethylenediamine or its hydrochloride is removed from the apparatus as an aqueous solution at 10, and the diamine compound is recovered from this solution, which also contains ammonium chloride.

The pressure prevailing in the apparatus will, of course, vary with the NH_3 concentration and temperature. This may be 110°C., corresponding to a pressure of the order of 10 atmos. In the presence of cuprous chloride, the reaction rate is accelerated.

Manufacture of Aniline from Chlorobenzene.



It is economically advantageous to conduct the manufacture of aniline from chlorobenzene in conjunction with the large-scale production of chlorine and chlorinated products, the introduction of cheap chlorobenzene into the aniline plant thus being permitted. With such a setup, this process competes favorably with the older method involving the reduction of nitrobenzene.

The toxic character of aniline vapors and the vicissitudes of industrial operations make it desirable to provide a fireproof housing with ample headroom and also adequate ventilation. It is, furthermore, customary to separate the high-pressure autoclave work from the subsequent separation and distillation operations. The autoclaves, which may be either vertical or horizontal, are ordinarily made of rolled steel. They are generally jacketed for use with high-pressure steam or a fluid heat-transfer agent. It is most important to provide thorough and turbulent mixing so that a uniform reaction mixture prevails.

Amination proceeds slowly under 160°C. and very rapidly at 210°C. At still higher temperatures, there is a distinct tendency to decomposition, and the increased pressure on the system makes gastight operation more difficult of attainment. A temperature range of 200 to 210°C. for the conversion of chlorobenzene to aniline gives very satisfactory results. At this temperature, with a 6:1 ammonia ratio of 28 per cent NH_3, the pressure on the system will be about 850 to 950 lb. per sq. in. The influence of temperature on the course of amination is shown in Fig. 12.[1]

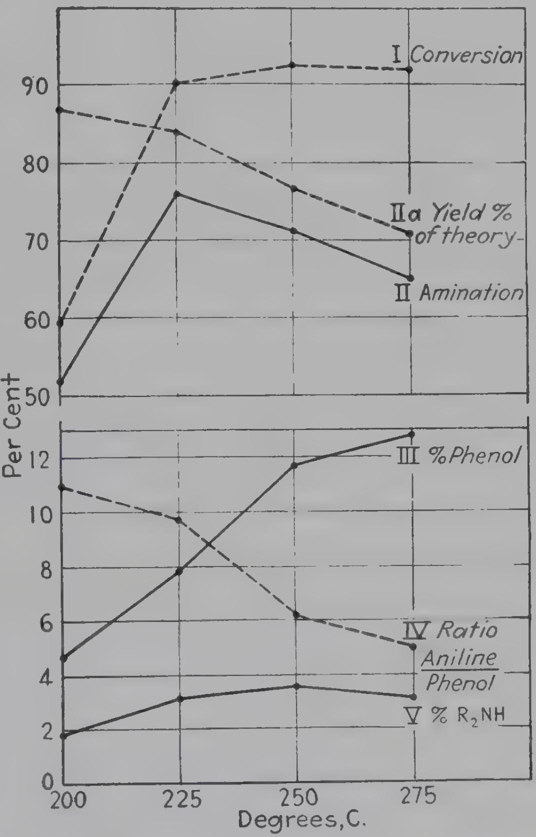


FIG. 12.—Ammonolysis of chlorobenzene: effect of temperature (freeboard 21 per cent). Time, 4 hr.; 0.2 mole Cu_2O; NH_3 (33%) ratio = 5.

The data in Table X show that an increase in the NH_3 ratio results in (1) a better yield of aniline; (2) an increase in the ratio of aniline to phenol; and (3) a slight diminution in the yield of diphenylamine.[1] These characteristics are especially marked in proceeding from 3 to 5 to 6 moles of NH_3 per mole of chlorobenzene. A further increase in the ratio of aqueous NH_3 has only a relatively small effect on the conversion and yield of aniline, and its use would only diminish the productivity of the autoclaves. When very small ammonia ratios are employed, there is not only a pronounced diminution in the NH_3 concentration of the liquor toward the end of the reaction, but there is also a corresponding increase in the NH_4Cl concentration which markedly retards the reaction.

The vapors leaving the reaction system are first expanded and then cooled below 100°C. in a suitable pipe condenser or dephlegmating column. Most of the ammonia continues to an absorption system in which the gas is recovered.

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[1] VOROZHTZOV and KOBELEV, *J. Gen. Chem.* (*U.S.S.R.*), **4**, 310 (1934).

Treatment of Autoclave Charge.—The aqueous aniline, containing some ammonia, unconverted chlorobenzene, phenol, and diphenylamine, as well as copper and ammonium compounds, is led to a still. Here the charge may be treated with a calculated quantity of alkali to (1) decompose the ammonium chloride; (2) convert the phenol to alkali phenoxide; and (3) precipitate the copper as a sludge upon the removal of the free ammonia. By distillation with steam, the ammonia, chlorobenzene, aniline, and diphenylamine are removed. The remaining aqueous portion, which contains dissolved sodium phenoxide, is filtered from the copper sludge and transferred to another vessel. The phenol is recovered from the acidified solution by distillation.

TABLE X.—PREPARATION OF ANILINE: EFFECT OF AMMONIA RATIO

0.2 Mole CuO per Mole Chlorobenzene. Operating Pressure 70 Atmos. = 980 Lb. per Sq. In. Size of Charge Adjusted for 21% Freeboard at Room Temp.

Mole ratio NH_3: chlorobenzene	Temp., °C.	Decomposition, %	Yield of aniline, % of theory		Yield of phenol, % of theory	Ratio of aniline to phenol	Yield of diphenylamine, % of theory
			% of C_6H_5Cl used	% of C_6H_5Cl which enters into the reaction			
3	187–244	89.1	78.3	87.8	5.2	15.1	1.7
4	188–239	98.5	89.0	90.5	5.3	16.8	1.8
3	193–242	84.2	72.2	85.7	5.5	13.1	1.5
4	193–237	95.5	83.5	87.5	5.5	14.8	1.9
5	192–230	99.1	88.2	88.9	5.6	15.8	1.5
6	196–229	99.6	89.8	90.2	5.5	16.6	1.0
8	194–222	99.5	90.0	90.4	5.2	17.3	1.0
12	192–215	98.2	90.6	92.3	5.0	17.9	0.0

According to Vorozhtzov.

An alternate and more economical procedure consists in cooling and settling the reaction mass from the autoclaves whereby the charge separates into two layers—a dark-brown lower layer, comprising principally aniline, and an almost colorless upper aqueous layer, which rapidly becomes blue on exposure to air. The volume of the water layer will, of course, be considerably greater than that of the aniline layer and will vary with the ammonia liquor ratio. When 5 moles of 32 per cent ammonia and 0.1 mole of cuprous oxide were used per mole chlorobenzene, Vorozhtzov found that the products of reaction were distributed as follows:

Aniline-layer components, % by weight	Substance	Water-layer components % by weight
81.55	Aniline	4.9
4.9	Phenol	0.33
0.85	Diphenylamine	None
Traces.........	Chloride ion (NH_4Cl)	8.84
Traces.........	Cu_2O	2.9
Traces.........	NH_3	13.8

To recover the aniline and other products, 50 per cent sodium hydroxide is added to the aniline-layer charge in an amount corresponding to 0.2 per cent of its volume. The batch is then subjected to fractional distillation using jacket heat. The first fraction is aniline water, and this is followed by a technically pure aniline of 97 to 99 per cent purity, which contains neither phenol nor diphenylamine. The weight of aniline thus recovered corresponds to 90 per cent of the amine originally present. After the removal of the aniline, the charge still contains sodium phenoxide and diphenylamine. The latter is separated by distillation with steam, while the phenol is recovered by acidifying the residue and distilling.

Alkali is also added to the water fraction in an amount sufficient to react with all ammonium compounds and with phenol. Upon fractional distillation, ammonia is first expelled and then recovered in a suitable absorption system. An aniline-water fraction is next distilled, from which an aniline layer separates out on cooling. The supernatant aqueous portion containing a small quantity of amine can be used in the NH_3 absorption system. The residual solution of sodium phenoxide and sodium chloride is then filtered from the precipitated copper oxides. The recovered copper oxide catalyst is washed and again used alone or with fresh copper in subsequent operations.[1]

2-Aminoanthraquinone from 2-Chloroanthraquinone.—The reaction is preferably carried out in a horizontal, jacketed autoclave provided with an agitator. The latter comprises a series of splash arms, which are designed to keep the top of the pressure vessel free of any unconverted halogeno compound. By employing a horizontal pressure vessel, this very important problem is readily solved, because the necessary freeboard can be obtained with a minimum of headroom. In vertical autoclaves, it is necessary to use a sleeve-and-turbine agitator, the turbine being instrumental in dragging the supernatant 2-chloroanthraquinone down through the sleeve into the ammoniacal solution.

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[1] Britton and Williams, U. S. 1,726,171 (1936).

By the use of potassium chlorate and ammonium nitrate as oxidants, it is possible to obtain directly a 2-aminoanthraquinone of 97.5 to 98.5 per cent purity. A copper catalyst is not essential but is sometimes used to moderate the conditions of the reaction. The only treatment required is a thorough washing of the 2-aminoanthraquinone with hot, dilute, aqueous ammonia or dilute sodium hydroxide.

By employing 7.5 parts of 28 per cent ammonia liquor per part of 2-chloroanthraquinone and heating at 200°C., the reactions can be completed in 24 hr.; at 210°C., only 15 hr. is required. It is advisable to fill the autoclave up to 75 per cent of its capacity with the aqueous ammonia in order to ensure against excessive freeboard.

TABLE XI.—EFFECT OF $KClO_3$-NH_4NO_3 MIXTURES IN AMMONOLYSIS OF 2-CHLOROANTHRAQUINONE

2-Chloroanthraquinone, 36.375 Gm. 28% NH_3 *Aq.*, 315 Gm. Capacity of Autoclave, 500 Cc.

Expt. No.	Binary mixture		Temp., °C.	Time, hr.	Yield, %	Purity, %	Net yield, %
	Materials	Gm.					
1	$KClO_3$	1.0	195	24	96.5	95.5	92.1
2	$KClO_3$ NH_4NO_3	1.0 8.0	195	24	96.5	97.7	94.3
3	$KClO_3$ NH_4NO_3	0.5 6.0	200	18	97.8	97.6	95.5
4	$KClO_3$ NH_4NO_3	0.5 6.0	200	18	97.8	98.0	95.8
5	$KClO_3$ NH_4NO_3	1.0 8.0	200	18	97.4	98.5	95.9

At the completion of the reaction, the ammonia vapor is vented to the absorbers until the residual pressure is about 200 lb. The charge is then delivered to a steel vessel containing dilute alkali, to decompose the combined ammonia. When the hot reaction product is brought in contact with the caustic solution, a finely divided brown product is obtained. When the product crystallizes out from its mother liquor in the autoclave, fine, long, purple-brown needles are obtained.

The ammonia is removed by distillation with steam, most of the hydroxy compounds going into solution as the sodium salt during this operation. The aminoanthraquinone is then filtered hot and washed with hot, dilute, alkaline solutions. Generally, no purification operation is required. The results obtained by the foregoing procedure are set forth in Table XI.

Preparation of *p*-Nitroaniline, in Jacketed Autoclaves.—A batch consisting of 500 lb. of molten *p*-nitrochlorobenzene and 2,600 lb. of 26°Bé. ammonia is introduced into a 500-gal. autoclave provided with an efficient stirrer. The ammonia liquor is run in first in order to prevent the formation of a mass of fused nitro compound at the base. The heating is at first very gradual, so that the operating temperature of 170°C., corresponding to a pressure of 500 to 550 lb. per sq. in., is not reached until after the expiration of 3 hr.

The heating of the autoclave is continued for 16 hr. at 170°C., at which time the conversion to amine is practically complete. Some of the ammonia gas is vented to the absorption system, and when the residual pressure on the autoclave has dropped to 200 lb., the pressure-relief line is closed, as it is then safe to effect a transfer of the charge from the autoclave to the ammonia still, by means of the residual autoclave pressure (see Fig. 13).

The still is usually a large steel vessel of 1,500-gal. capacity, which can conveniently hold two autoclave charges under ordinary conditions and a third one in case of an emergency. It is provided with an agitator, gas line to the ammonia absorbers, and vent to the atmosphere, the latter enabling the operator to determine when the removal of ammonia is complete.

When all the ammonia has been removed from the still, the lines to the absorbers are closed, and the steam pressure on the kettle brought up to 60 lb. The charge is then passed through a pressure filter.

The crystallizing tubs are large wooden vats provided with wooden stirrers. They are tightly covered and provided with wooden flumes which serve to remove the toxic vapors. As a result of the sudden drop of both temperature and pressure, the *p*-nitroaniline, on entering the tub, immediately crystallizes out of solution as a very finely divided canary-yellow product.

Through a process of condensation, 4, 4′-dinitrodiphenylamine is produced as an impurity. Being a secondary amine, it does not diazotize; consequently, when the *p*-nitroaniline made by this process is diazotized in the course of preparing lakes or dyestuffs, it will be observed that a flocculent precipitate consisting of approximately 0.3 per cent of the total product will remain in suspension as an inert solid impurity. This characteristic at one time was a powerful influence militating against a universal acceptance of this product, despite the fact that its purity averages 99 per cent. In order to remove this objectionable characteristic, recourse may be had to the use of mild reducing agents. The reductoactive material is placed in the crystallizing tubs prior to the entry of the charges from the filter press. These agents, by acting on the small amount of dinitrodiphenylamine that is present, serve to effect a distinct

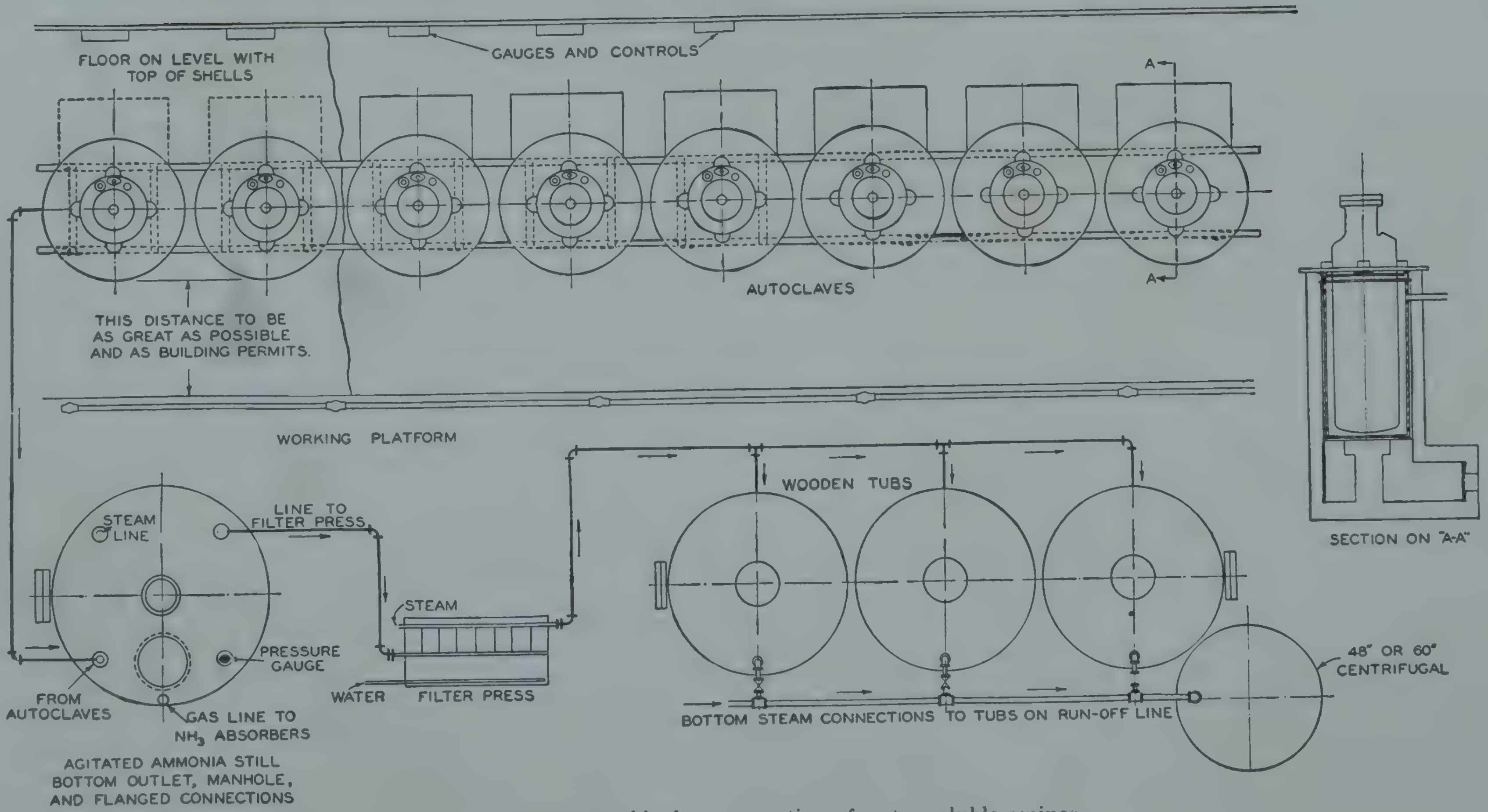
GAUGES AND CONTROLS
FLOOR ON LEVEL WITH TOP OF SHELLS
A
A
AUTOCLAVES
THIS DISTANCE TO BE AS GREAT AS POSSIBLE AND AS BUILDING PERMITS.
SECTION ON "A-A"
WORKING PLATFORM
WOODEN TUBS
STEAM LINE
LINE TO FILTER PRESS
STEAM
PRESSURE GAUGE
FROM AUTOCLAVES
GAS LINE TO NH$_3$ ABSORBERS
WATER
FILTER PRESS
BOTTOM STEAM CONNECTIONS TO TUBS ON RUN-OFF LINE
48" OR 60" CENTRIFUGAL
AGITATED AMMONIA STILL BOTTOM OUTLET, MANHOLE, AND FLANGED CONNECTIONS

FIG. 13.—Plant assembly for preparation of water-soluble amines.

improvement in the clarity of the diazonium solution of the *p*-nitroaniline thus treated. A similar improvement can be effected by recrystallizing the amine under pressure from weakly ammoniacal solutions, the enolized dinitro compound staying in solution.

The charge in the crystallizing tub is cooled at 30°C. and is then delivered by gravity to a centrifugal. The mother liquor leaving the centrifugal flows to an elaborate system of catch boxes, where it is cooled to room temperature. Periodically, the water in the catch boxes is syphoned out to enable the settled *p*-nitroaniline to be removed.

p-NITROANILINE OPERATING BUDGET
Steam-jacketed Autuclaves
SOURCES OF LOSS OF *p*-NITROANILINE

Operations Involved	Loss in Yield, %
1. Impurities in *p*-nitrochlorobenzene, including losses in transfer	1.0
2. Charging, autoclaving, filtering	0.5
3. Wash waters and centrifugal operations	1.0
4. Mother liquor and cleaning catch boxes	2.0
5. Drying and packaging	0.5
Total calculated loss in yield	5.0
Per cent yield of theory for good operations	95.0[1]

SOURCES OF LOSS OF AMMONIA LIQUOR

Operations Involved	Percentage of Total Loss
1. Delivery to operation system, including storage losses.	0.5
2. Charging and discharging of autoclaves	0.5
3. Free and combined NH_3 left in mother liquor	1.0
4. Losses in absorber system	2.0
5. Leaky stuffing boxes and operating losses	2.0
Total operating loss of NH_3	6.0[2]

[1] Recent small-scale operations show that yields of 96 to 97 per cent of the theoretical are possible.

[2] This figure does not, of course, include the ammonia entering into the reaction. The NH_3 consumed in the reaction is usually based on the *p*-nitroaniline delivered. This is obviously high, for the preceding data on *p*-nitroaniline losses show that some of the amine that consumed NH_3 in its preparation was lost in process.

Preparation of *p*-Nitroaniline in a Steel Cylinder.—In order to obviate the necessity of employing a hydraulic accumulator to regulate the internal pressure in the tubular coil system and to provide a means of examining the walls of the pressure system, Saunders has suggested the use of the apparatus shown in Fig. 14 for the manufacture of *p*-nitroaniline.[1] Here, the preheated aqueous ammonia is forced into the cylinder by means of pipe 11 and flows down to the bottom of the reaction vessel through the duct 14 and then passes upward inside the central annular tube. As the liquor rises upwardly through the packing 12, it meets a countercurrent flow of the heavier *p*-nitrochlorobenzene, which is forced into the system in a liquid condition and distributed by the plate 13. The reaction products overflow into a central tube of comparatively small bore and are removed at the bottom of the cylinder.

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[1] Saunders, U. S. 1,911,717 (1933).

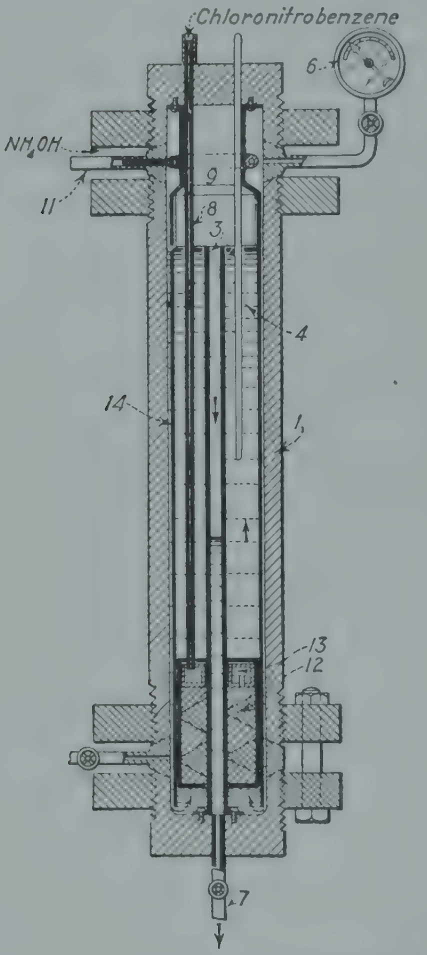


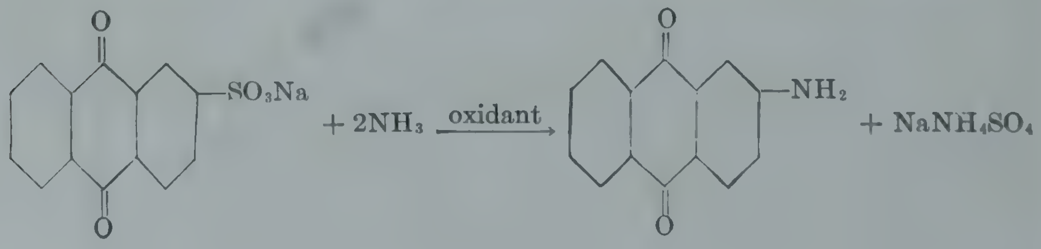
Fig. 14.—Apparatus for continuous aminations.

1. Pressure cylinder.
3. Overflow for finished product.
4. Annular reaction zone.
6. Pressure gauge.
7. Outlet for finished product.
8. Inlet tube for *p*-nitrochlorobenzene.
9. Pyrometer.
11. Ammonia-liquor inlet.
12. Packing in reaction zone.
13. Distributor plate.
14. Duct for ammonia liquor.

It is to be noted that in this system there is provided an upper vapor phase, which takes up the fluctuations in internal pressure, as in the operation of ordinary autoclaves.

For the preparation of *p*-nitroaniline, 150 to 200 parts of liquid *p*-nitrochlorobenzene preheated to 225°C. is delivered to every 900 parts by weight of 26°Bé. ammonia liquor. The reaction with heated ammonia takes place in the area provided with packing. The walls of the reactor in this section are made of or lined with stainless steel, to minimize the corrosive action of the ammonium chloride or hydrochloric acid that is split off. The operating pressure is approximately 1,200 lb. per sq. in. The rate of feed of the reactants is so regulated that practically all the *p*-nitrochlorobenzene is converted to amine. The reaction product escaping from the system is transferred to a still where the excess of ammonia is removed and the *p*-nitroaniline treated in any desired manner.

2-Aminoanthraquinone from Sodium Anthraquinone-2-Sulfonate.



The preparation of 2-aminoanthraquinone from *silver salt* presents no particularly difficult technical problems. Compared with the preparation of the amine from 2-chloroanthraquinone, this reaction may be carried out under distinctly milder conditions. The reactants NH_3 and anthraquinone-2-sulfonic acid (Na salt) are both present in aqueous solution, and the conversion to amine takes place readily.

As the reaction progresses, the amino compound separates out as a light, golden-brown product. The 2-aminoanthraquinone obtained by this process generally averages 99 per cent pure, by titration with sodium nitrite. The yields range from 90 to 94 per cent of the theoretical. Copper and its salts are not necessary, the best results being obtained by employing the technic involving the use of oxidants and the ammonium salts of oxidizing acids.

A number of important technical and economic considerations are involved in the use of sodium anthraquinone-2-sulfonate (*silver salt*) for the preparation of 2-aminoanthraquinone. The cost of chloroanthraquinone is approximately the same as anthraquinone when they are prepared according to the Friedel–Crafts' reaction. The former lends itself to the direct production of an amine of 97 to 98.5 per cent purity. The product from "silver salt" is, however, of a higher purity and can, furthermore, be prepared at a lower operating temperature, *viz.*, 170 to 180°C., so that steam-jacketed equipment can be employed. Consequently, despite economic handicaps, the silver-salt process is firmly entrenched and is used to a considerable extent.

When anthraquinone-2-sulfonic acid is made by the sulfonation of anthraquinone according to traditional methods, its cost would be distinctly higher than that of 2-chloroanthraquinone because of extra operating steps and the fact that disulfonic acids are formed during the sulfonation process. The cost of production may be somewhat lowered by cyclizing the intermediate benzoylbenzoic acid with 96 per cent sulfuric acid at 130°C. and then sulfonating the anthraquinone thus formed by the addition of oleum. Another and more economical method involves the conversion of 4′-chloro-2-benzoylbenzoic acid to the sulfonic acid derivative by treatment with sodium sulfite under pressure and then[1] cyclizing the sulfobenzoylbenzoic acid to anthraquinone-2-sulfonic acid. It is clear that this process results solely in the formation of "*silver salt*," and experience shows that the yields are good and that it can be converted to 2-aminoanthraquinone of high purity.

β-Naphthylamine from β-Naphthol.—When β-naphthol is treated with an excess of aqueous ammonia at 200°C., the yield of β-naphthylamine obtained is only about 75 per cent of theory. Bucherer discovered that the amination could be carried out much more satisfactorily and at greatly reduced pressures by introducing ammonium sulfite into the reaction mass.[1] In the presence of ammonium sulfite, the sulfite addition compound of β-naphthol is formed and converted to amine in the presence of an excess of strong ammonia, ammonium sulfite being split off (see page 359). The sulfite is thus instrumental in producing a compound of greater dissociating power and in this way serves as a catalyst.

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[1] Thomas and Dresher, U. S. 1,779,221 (1930).

The ammonolysis is carried out in jacketed, agitated autoclaves. Such equipment is essential, as it is necessary to obtain a uniform temperature control in order to inhibit the formation of 2, 2′-dinaphthylamine, which is appreciable above 150°C.; whereas the conversion to amine below this temperature does not progress readily, and considerable unconverted material remains in the charge. As in the preparation of *p*-nitroaniline, it is necessary to provide a stirrer to keep the β-naphthol in suspension in the ammoniacal liquor.

The autoclave batch consists of molecular quantities of β-naphthol and ammonium sulfite and 720 lb. of 28 per cent ammonia to provide a 12:1 NH_3 ratio to the 144 lb. of hydroxy compound taken. The charge is heated at 150°C. for 8 hr., after which it is blown to a still containing an alkali solution. Here the ammonia may be distilled off and recovered, as in the case of *p*-nitroaniline. In this way, the ammonia liquor entering the system is kept uniformly pure. The ammonium sulfite is converted to the alkali salt and is removed in an impure state with the mother liquor. An alternative and more economical method consists in cooling the autoclave charge under agitation. The finely granulated mass of β-naphthylamine obtained is filtered from its ammoniacal mother liquor. The filtrate, which contains the ammonia and ammonium sulfite in approximately the desired proportions, may be again used, after clarifying with a filter aid and strengthening the NH_3 content. The β-naphthylamine on the filter is washed free of unconverted β-naphthol with hot dilute caustic soda. The amine is then delivered to a vat, in which it is taken up with 300 lb. of warm 15 per cent hydrochloric acid which is free of H_2SO_4. Any remaining β-naphthol is removed by filtering this acid solution. The yield is about 85 per cent.

A pure product may be obtained by neutralizing the solution with sodium carbonate, evaporating to dryness, and then distilling the dry base at 25 mm. pressure. The purification may also be made by treating the β-naphthylamine hydrochloride with 200 lb. of sodium sulfate, whereby naphthylamine sulfate is precipitated out. The precipitate is stirred for several hours and allowed to settle. It is then filtered and washed with cold water. The free base is obtained by treating the powdered sulfate with a strong, hot sodium carbonate solution. The final product is cooled, filtered, and washed free of alkali, after which it is dried in an air drier.

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[1] BUCHERER, *J. prakt. Chem.*, **69**, 88 (1904). This subject matter became public five years previously in Ger. 117,471 (1899); 121,683 (1901). The reaction is generally referred to as the Bucherer reaction.

Amination of 2-Hydroxynaphthalene-3-carboxylic Acid. *Liquid Phase: in the Presence of a Metal Catalyst.*—According to Fierz and Tobler, the preparation of 2-aminonaphthalene-3-carboxylic acid may be carried out as follows: 250 parts of zinc chloride is dissolved in 300 parts of water, and the solution then introduced into an autoclave provided with a stirrer and treated with 500 parts of 2-hydroxynaphthalene-3-carboxylic acid.[1] The autoclave is then closed, and 120 to 140 parts of gaseous ammonia is introduced into it. The whole is heated for 24 hr. at 220 to 230° (temperature of the oil bath), an operation that produces a pressure of 12 to 20 atmos. The reaction mixture forms a rather thick yellow mass, which is boiled with 4,000 parts of water and 1,400 parts of concentrated hydrochloric acid, whereby almost complete solution occurs. The hot solution is filtered, and the filtrate treated with 1,200 to 1,500 parts of common salt and allowed to cool. A compound containing 2-aminonaphthalene-3-carboxylic acid—probably as an inner salt or amide—separates as colorless crystals. The latter are filtered, washed with a saturated salt solution, dissolved in 7,000 parts of a solution of sodium carbonate of 8 per cent strength, and filtered. The free 2-aminonaphthalene-3-carboxylic acid may be precipitated from the alkaline filtrate by addition of acid, or the solution may be worked up directly. Yields above 80 per cent of theory are obtainable.

Conversion of Alcohols to Alkylamines.[2,3,4] *Preparation of Methylamines.*—Monomethylamine is formed with only minor proportions of di- and trimethylamines by passing methanol and ammonia, in a ratio of 1:5, over alumina gel at a rate of 0.75 to 1.5 cc. per cubic centimeter of catalyst per hour. The vapors are preheated to about 350°C., and the catalyst is kept at 450°C. About 13.5 per cent of the ammonia is thus converted to primary amine. Secondary and tertiary amines are formed in amounts representing 7.5 and 10.5 per cent, respectively, of the ammonia. The secondary and tertiary amines can be separated from the primary amine and recirculated over the catalyst with fresh methanol and a large excess of ammonia, thus increasing the proportion of primary amine and materially decreasing the proportion of secondary and tertiary amines.

It is difficult and often uneconomical and impracticable to arrange operating conditions for the production of one of the amines. It is customary, therefore, to rework the products under suitable conditions or to reintroduce them into the amination system along with fresh reactants.[1,2] Swallen and Martin have shown that primary methylamine can be converted to dimethylamine and trimethylamine by repassing it through the catalytic chamber in the absence of ammonia.[1] The results obtained when methylamine and various mixtures of it were passed over a partially dehydrated aluminum trihydrate catalyst are set forth in Table XII.

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[1] Fierz and Tobler, U. S. 1,629,894 (1925).

[2] Arnold, U. S. 1,799,722 (1931).

[3] Martin and Swallen, U. S. 1,875,747 (1932).

[4] Andrews, U. S. 2,073,671 (1937).

TABLE XII.—EQUILIBRIUM STUDIES: PREPARATION OF METHYLAMINES

Composition of feed	Temp., °C.	Space velocity, $\frac{\text{cc. gas}}{\text{cc. catalyst}}$	Composition of product			
			NH_3, %	CH_3NH_2, %	$(CH_3)_2NH$, %	$(CH_3)_3N$, %
100 % CH_3NH_2	450	550	33.2	31.8	31.4	3.6
	450	550	31.8	31.3	32.6	4.3
87.0 % CH_3NH_2 13.0 % $(CH_3)_3N$	425	400	27.0	25.3	33.1	15.6
	425	400	25.4	29.8	27.7	17.1
	450	670	35.2	27.6	24.4	12.9
	450	630	39.0	33.6	16.3	11.1
	450	550	29.2	26.5	29.8	14.5
	450	550	30.4	26.4	28.6	14.6
	475	510	40.0	28.2	16.4	15.3
	475	420	38.0	26.6	17.4	18.0
65.0 % CH_3NH_2 20.2 % $(CH_3)_2NH$ 14.8 % $(CH_3)_3N$	450	680	38.6	23.6	17.4	20.4
	450	350	32.0	25.8	26.2	15.9

According to Swallen and Martin.

The reworking or recycling of unwanted amines to afford a greater yield of desired product is generally effective. Obviously, the results are more striking in the preparation of alkyl- and alkanolamines where, in addition to primary amines, the formation of secondary and tertiary amines occurs in substantial quantities. This is particularly true when, in the interest of economy, moderate NH_3 ratios are employed. Evidence of a corresponding mechanism in the similar synthesis of arylamines is available, although here primary amines can be obtained almost exclusively.

When dimethylamine is the desired product, the unwanted amines are separated by fractionation and recycled along with fresh materials.

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[1] Herold and Smeykal, U. S. 2,068,132 (1937).

[2] Swallen and Martin, U. S. 1,926,691 (1933).

he data below show that only a negligible change occurs in the perentage of mono- and trimethylamines, practically all the added methanol eing converted to dimethylamine.[1] The excess of ammonia is separated

Constituent	Charge wgt., %	Products wgt., %
Ammonia	28.4	25.7
Monomethylamine	12.0	10.6
Dimethylamine	0	18.0
Trimethylamine	39.7	38.2
Methanol	19.9	0

nder pressure (Fig. 15) during the course of the operations and is ondensed and reused. The higher alkylamines are made in a similar anner.

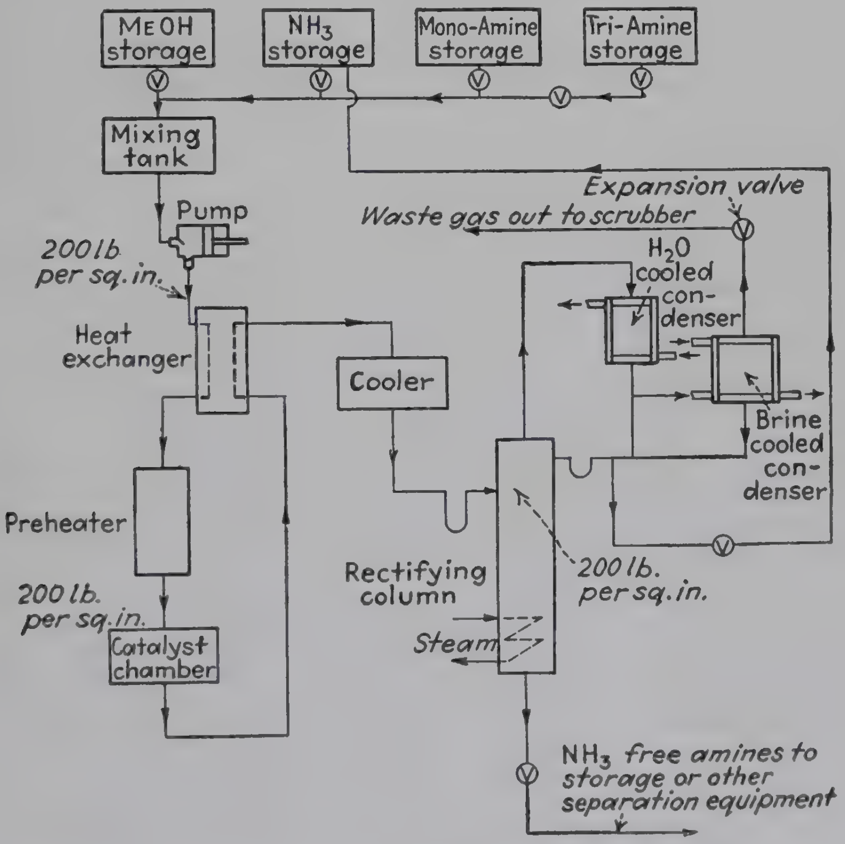
MeOH storage
NH₃ storage
Mono-Amine storage
Tri-Amine storage
Mixing tank
Pump
200 lb per sq. in.
Heat exchanger
Preheater
200 lb. per sq. in.
Catalyst chamber
Cooler
Expansion valve
Waste gas out to scrubber
H₂O cooled condenser
Brine cooled condenser
Rectifying column
200 lb. per sq. in.
Steam
NH₃ free amines to storage or other separation equipment

FIG. 15.—Flow diagram; preparation of dimethylamine.

The alkylamines can generally be separated from one another by areful fractionation. In the case of methylamines, this problem is difficult because of the closeness of the boiling points, as can be seen from the data below.

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[1] Greenwalt, U. S. 2,098,289 (1937).

PROPERTIES OF ETHYL- AND METHYLAMINES

Substance	B.p., °C.	Sol.: H_2O, gms./100 cc.	Diss. const.
$C_2H_5NH_2$	16.5	∞	0.00056
$(C_2H_5)_2NH$	55.9	81.5	0.00126
$(C_2H_5)_3N$	89.5	1.5	0.00064
CH_3NH_2	−6.8	Sol.	0.00047
$(CH_3)_2NH$	7.4	Sol.	0.00102
$(CH_3)_3N$	3.5	V. sol.	0.00055

The problem of separating the methylamines is further complicated by the presence of unreacted ammonia, methanol, and impurities such as carbon dioxide and formaldehyde. It has been found that when the reaction mixture is thoroughly mixed with a solution of an inorganic base—such as sodium hydroxide—before distillation, the impurities form water-soluble salts and the separation of the amines is facilitated.[1]

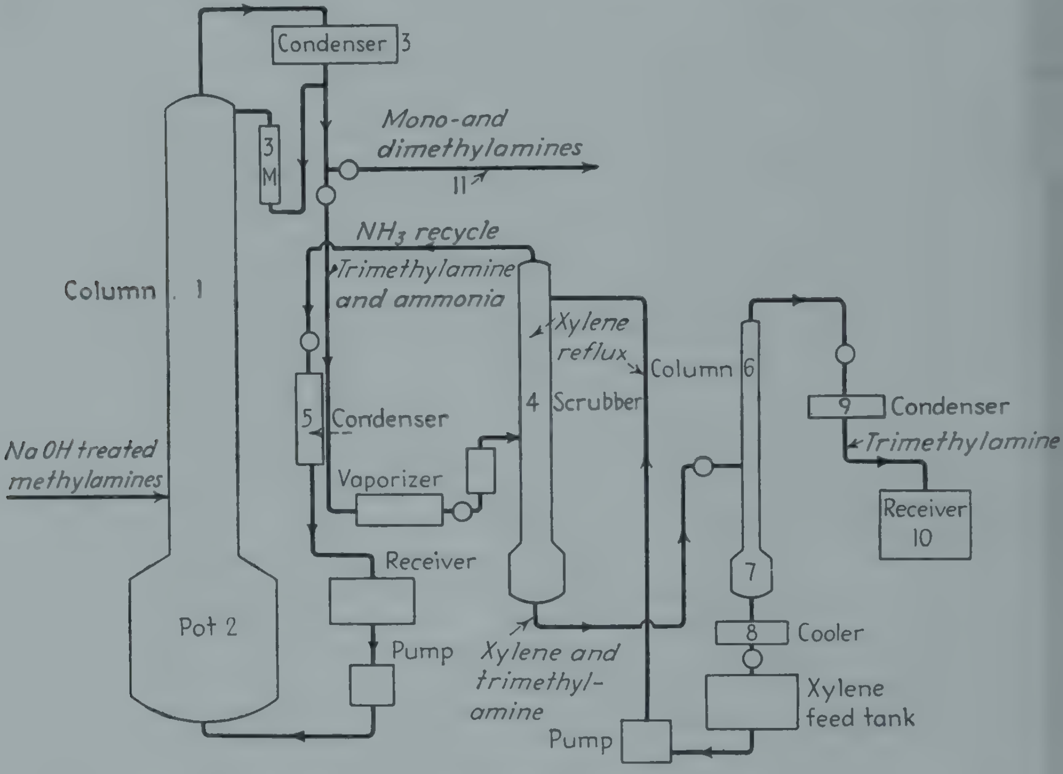
Condenser 3
3 M
Mono-and dimethylamines
11
NH_3 recycle
Trimethylamine and ammonia
Column 1
Xylene reflux
Column 6
9 Condenser
Trimethylamine
Receiver 10
4 Scrubber
5 Condenser
Vaporizer
NaOH treated methylamines
Receiver
Pot 2
Pump
Xylene and trimethylamine
Pump
7
8 Cooler
Xylene feed tank

FIG. 16.—Separation of methylamines.

The crude methylamines leaving the catalyst chamber and cooler (Fig. 16) are washed countercurrently under a pressure of 225 lb. per sq.

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[1] Olin, U. S. 2,377,511 (1945).

in. with a 10 to 12 per cent caustic soda solution introduced on the upper plates of the rectifying column. The amines that leave the top of the column are thus cooled from about 165 to 90°. The vapors are condensed and partially freed of impurities and then delivered to column 1 (Fig. 16). Here ammonia is added (122 parts NH_3 to 325 parts of combined methylamines), and an azeotropic mixture of ammonia and trimethylamine is distilled overhead. A good reflux is maintained in this column by proper adjustment of the temperature in pot 2 and the cooling water in condenser 3. Part of the condensate is used as a reflux, returning to the column via the reflux meter 3*M*, while the remainder is passed through a vaporizer and meter to the central portion of scrubber 4, which is maintained at 225° and 200 lb. per sq. in. pressure. Xylene is continuously fed near the top of the scrubber to extract the trimethylamine selectively. Ammonia containing a small amount of trimethylamine is removed overhead and led to a condenser 5 and is then pumped to pot 2 for further removal of trimethylamine.

The xylene solution of trimethylamine is withdrawn at the base of the scrubber 4 and delivered to column 6, operated at a gauge pressure of 50 lb. per sq. in., where the trimethylamine is separated from the solvent by distillation. The solvent is here removed as a condensate from pot 7 and cooler 8, while the crude trimethylamine containing a small amount of ammonia passes overhead to a condenser 9 from which it flows to a receiver 10. Upon redistillation, an overhead azeotropic mixture of ammonia and trimethylamine is obtained, the residue being substantially pure trimethylamine.

When the concentration of trimethylamine in the distillate from column 1 is reduced to less than 5 per cent, the valves to scrubber 4 are closed, the mono- and dimethylamines and ammonia are separated from each other by distillation, and the distillate leaving condenser 3 goes through line 11 to appropriate receivers. With the use of the preceding technic, the following cuts were obtained on the distillation of 325 parts of a crude methylamine mixture:

Cut No.	Weight, lb.	Methylamine in fraction
1	90.5	NH_3 containing 6% $(CH_3)_3N$
2	26.5	NH_3 and CH_3NH_2
3	34.0	CH_3NH_2(98% pure)
4	45.5	CH_3NH_2 and $(CH_3)_2NH$
5	89 5	$(CH_3)_2NH$(99 plus % pure)

Preparation of Butylamines.—The liquid-phase amination of butanol and butanone-2 to the corresponding normal and secondary amines can be carried out in equipment similar to that shown in Fig. 17.[1] In the conversion of the ketone, 1,440 parts by weight of methyl ethyl ketone, 82 parts of a Raney nickel catalyst, and 400 parts of secondary butyl alcohol are introduced through line 1 into the jacketed autoclave 2. The mixture undergoing agitation in the autoclave is saturated with 490 parts of ammonia under a total pressure of 100 lb. per sq. in. Part of this pressure is obtained by heating the ammonia in a jacketed cylinder 3, which is connected to the autoclave by means of line 4. The temperature of the reaction mass is then raised to 150° by passing steam through the autoclave jacket. Hydrogen is then introduced through line 1 and maintained at a pressure of 1,000 lb. per sq. in. The rapid absorption of hydrogen is accompanied by an appreciable evolution of heat, and the temperature rises to about 170 to 190°.

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[1] Davy, U. S. 2,312,754 (1943).

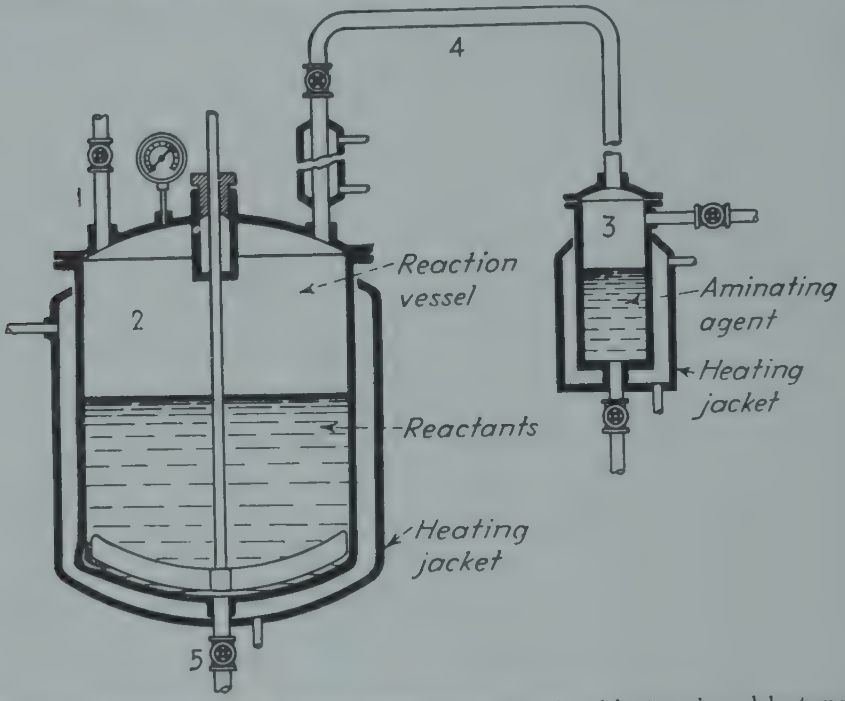


FIG. 17.—Apparatus for liquid-phase ammonolysis of butanol and butanone.

1. Feed line for alcohol, ketone, catalyst, and hydrogen.
2. Pressure autoclave with jacket, stirrer, and gauges.
3. Pressure cylinder for ammonia.
4. Ammonia delivery line.
5. Drawoff for amino compounds.

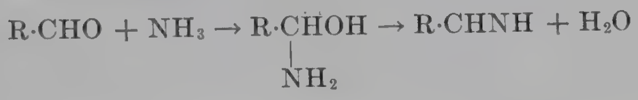
The temperature and pressure in the autoclave are then maintained for 2 hr., after which the ammonia, along with some hydrogen, is released to a cooled vessel. The product is removed through line 5 and distilled in a tall helix packed column employing a 20:1 reflux ratio. The following fractions are obtained:

Cut No.	Temp., °C.	Secondary butylamine obtained, parts
1	64	1,307 (98.5% pure)
2	64–70	30 (71.0% pure)
3	70–84	53 (36.3% pure)

The total weight of amine produced is 1,328 parts, or 91 per cent. When secondary butyl alcohol is not used as a solvent, the yield is only about 65 per cent.[1]

The liquid-phase ammonolysis of butyl alcohol can be carried out under substantially the same conditions as noted above without the use of a solvent. As stated previously (page 363), the ammonolysis of butanol can also be carried out in the vapor phase, either in the presence of a dehydration catalyst or in conjunction with hydrogen and a hydrogenation catalyst.

Ammonolysis of Aldose Sugars. *Preparation of Aldehyde-ammonia Addition Compound.*—When aldose sugars are heated with ammonia under moderate pressures, the hydroxylamino addition compound is formed. Further treatment under more drastic conditions results in the elimination of the elements of water with formation of an aldosimine.



$$R{\cdot}CHO + NH_3 \rightarrow R{\cdot}\underset{\substack{|\\ NH_2}}{C}HOH \rightarrow R{\cdot}CHNH + H_2O$$

The glucose-ammonia addition compound is formed by introducing 150 parts of anhydrous glucose in a stainless-steel autoclave and adding 122 parts of liquid NH_3 to the precooled charge at below −40°. The autoclave is sealed, and the agitated charge is heated to 60° in 1 hr. The temperature is maintained at this point for about 2 hr.; and after cooling, the ammonia pressure is released.

The reaction product is a brown sirup, which, after being triturated with anhydrous ethanol, yields 63 parts by weight of white crystalline glucose ammonia. The reaction product has a nitrogen content of 5.8 per cent compared with the theoretical of 7.1 for the aldehydeammonia of glucose.

The preparation of glucosimine is effected by charging an autoclave with 250 parts of anhydrous glucose and 600 parts by weight of anhydrous methanol. After cooling to about −40°, ammonia gas is passed into the mixture. The autoclave is then sealed, and the agitated charge is heated to 72° and maintained at that temperature for about 3 hr. The resultant pressure of 160 lb. per sq. in. is released, and the charge transferred. The product is a clear amber solution from which white crystals of glucosimine are obtained on cooling. The crystalline material amounts to 80 parts by weight and has a nitrogen content of 7.6 compared with the theoretical N content of 7.8 for glucosimine.

When the ammonolysis is carried out in the presence of hydrogen and a hydrogenation catalyst, the aldose sugars yield the corresponding *aldosamines.* Conjoint amination reduction is necessary for the replacement for carbonyl groups. The preparation of *glucosamine* may be carried out as follows:[1] Twenty five hundred grams of commercial glucose is charged into an autoclave containing 2,500 gm. of 21 per cent aqueous ammonia and 250 gm. of a reduced nickel catalyst. Hydrogen is then introduced until a pressure of about 100 atmos. is obtained, and the charge is stirred without heating for ½ hr. to effect solution of the glucose. With the application of heat, hydrogen absorption begins at 63 to 65°C., and the temperature is brought up to 95°C. Hydrogen is introduced periodically during a ½-hr. period to replenish that consumed in the reaction. The charge, which is then free from reducing sugars, is filtered and concentrated. Glucosamine is obtained in good yields as a viscous noncrystalline sirup. From the anhydrous sirup, glucosamine can be crystallized out of methanol as a white crystalline compound melting at 127°C.

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[1] Olin, U. S. 2,278,373 (1942).

Preparation of Amino Derivatives of Fatty Acids.—The two principal methods of preparing amino derivatives of fatty acids are (1) the replacement of halogen, as in the conversion of chloroacetic acid to glycines and α-bromostearic acid to the corresponding primary and secondary amino compounds, and (2) the conjoint amination reduction of keto fatty acids and their amides.

Alpha-aminostearic acid is prepared by the reaction of the corresponding bromo derivative with ammonia. In a similar manner, the *mono- and dialkylamino compounds* can be obtained by the use of an alkylamine with a replaceable hydrogen as the aminating agent.[2] The preparation of alpha-dimethylaminostearic acid is carried out by adding crude or pure α-bromostearic acid (744 parts) to 97 parts by weight of dimethylamine dissolved in a sodium hydroxide solution consisting of 587 parts of 30 per cent caustic soda and 1,085 parts of water. The molten or shredded α-bromostearic acid is fed in gradually at 15 to 20° in a period of 1 hr., and the agitated reaction mass is allowed to warm up to 25° over a period of 6 hr. The temperature of the charge is then increased to 35°, and stirring is continued for 12 hr. After contents of the vessel are allowed to stand for about 6 days, an almost quantitative yield of crude α-dimethylaminostearic acid is obtained.

During the prolonged period of agitation, the nonhomogeneous mixture changes to a stable, clear, amber, sirupy liquid. The aqueous paste of sodium α-dimethylaminostearate, which forms clear solutions in water and dilute hydrochloric acid, is a good detergent and textile-softening agent.

Preparation of 12-Aminostearic Acid.[3]—A mixture of 100 parts by weight of 12-ketostearic acid, 330 parts of methanol, 300 parts of water,

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[1] Flint and Salzberg, U. S. 2,016,962 (1935).

[2] Henke and Schofield, U. S. 2,279,138 (1942).

[3] Hanford, U. S. 2,312,967 (1943).

14.5 parts of caustic soda, 1.7 parts of ammonium chloride, and 17 parts of an alloy-skeleton nickel catalyst are placed in a reaction vessel. After the addition of 85 parts anhydrous ammonia (molar ratio NH_3 to keto acid 15:1), the reaction mixture is heated at 150° for 2 hr. Hydrogen is then introduced for 3 hr. at an initial pressure of 2,000 lb. per sq. in. The reaction mixture, while still hot enough to provide a clear solution, is transferred, and the suspended catalyst removed by filtration.

The filtrate is diluted with water to a volume of 8,300 parts, and dilute acetic acid is added while stirring until the solution is neutral. The crude 12-aminostearic acid thus precipitated is removed by filtration. Recrystallization from 80 per cent *tert*-butanol yields 62 parts of 12-aminostearic acid melting at 128 to 133°. A pure amino acid (m.p., 137 to 138°) is obtained by reprecipitation from aqueous formic acid solution.

Preparation of 12-Ketostearamide.—A well-stirred mixture of 100 parts of castor oil and 10 parts of nickel-on-kieselguhr catalyst is treated with hydrogen in an autoclave for 1 hr. at a temperature of 130° and a pressure of 2,000 lb. per sq. in. to effect the conversion of ricinolein to hydroxystearin. The pressure is gradually released to atmospheric, and dehydrogenation of 12-hydroxystearin to 12-ketostearin is accomplished by raising the temperature and heating at 275° for 6 hr.

The autoclave temperature is lowered, and 50 parts of anhydrous ammonia is then added. When the reaction mixture is heated at 150° for 8 hr., the ester is decomposed and 12-ketostearamide is formed. A pressure of 800 to 1,000 lb. per sq. in. is developed which is vented through an overhead discharge line at the end of the reaction. The molten ketostearamide is transferred and then purified by treating with decolorizing carbon and filtering. On recrystallization from ethanol, large, white, waxy flakes of 12-ketostearamide are obtained.

Conversion of 12-Ketostearamide to Amino Derivative.—A mixture of 100 parts by weight of ketostearamide, 15 parts of nickel catalyst, 1.7 parts of ammonium chloride, and 213 parts of methanol are placed in a stainless-steel autoclave fitted with a stirrer. Anhydrous ammonia (67 parts) is added, and the stirred reaction mass is heated to 130°. Sufficient hydrogen is introduced to maintain a pressure of 1,500 to 1,700 lb. per sq. in., and the reaction is continued for 2 hr. The autoclave charge is then cooled and transferred, and the nickel catalyst separated by filtration. The methanol solution is then added to 1,500 parts of water, while stirring, and the precipitated 12-aminostearamide is separated by filtration. The crude product is treated with a solution of 67 parts of glacial acetic acid in 1,000 parts of water, and the insoluble material removed by filtration.[1] A slight excess of 28 per cent aqueous ammonia is added to the well-stirred acetic acid solution of the amine to reprecipitate the 12-aminostearamide. On recrystallization from methanol, 60 parts of 12-aminostearamide (m.p., 86 to 88°) is obtained per 100 parts of keto acid used. It is a white microcrystalline powder which is soluble in aqueous organic acids and hot aqueous *tert*-butanol.

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[1] U. S. 2,283,683 (1942).

In a similar manner, 9(10)-hydrostearic acid derived from oleic acid by treatment with concentrated sulfuric acid at 10 to 15° can be converted successively to the corresponding methyl ester, methyl 9(10)-ketostearate, 9(10)-ketostearamide, 9(10)-aminostearamide, and 9(10)-aminostearic acid.

Preparation of Beta-Alanine.—Previously it was shown that β-aminopropionic acid (β-alanine) could be derived from a number of cyano compounds by ammonolysis. The processes involve the replacement of —OH and alk-OH groups as well as addition reactions. Aqueous ammonia is generally employed, and this medium serves to hydrolyze nitriles and esters, such as aminopropionitrile and methyl acrylate, to the desired carboxylic acid.

Replacement of —OH is exemplified by the conversion of ethylene cyanhydrin. A solution of 20.8 lb. of ethylene cyanhydrin and 202 lb. of 20 per cent aqueous ammonia is heated at 195° for 4 hr. in a pressure vessel. The product is treated with a decolorizing carbon, cooled, and filtered. The filtrate is evaporated to a sirupy consistency and is then diluted with 3 gal. of methanol. A 29 per cent yield of crystalline β-alanine is thus obtained.

When the filtrates resulting from the separation of β-aminopropionic acid are again treated with aqueous ammonia at 200°, the yield is increased by about 20 per cent. It appears that an equilibrium is reached in the reaction between ethylene cyanhydrin and aqueous ammonia; and by reworking the filtrates, fairly high yields are obtainable. Instead of ethylene cyanhydrin,[1] β-methoxypropionitrile,[2] $CH_3OC_2H_4CN$, and β, β′-dicyanoethyl ether,[3] $NC—C_2H_4—O—C_2H_4—CN$, can be used as starting materials.

When acrylonitrile is treated with ammonia, β-aminopropionitrile is obtained by addition.[4] Upon further treatment with aqueous ammonia, β-alanine is formed.

$$CH_2{=}CHCN + NH_3 \rightarrow H_2NCH_2CH_2CN \xrightarrow{NH_3\ aq.} H_2NCH_2CH_2COOH$$

Thus, 66.5 parts (1.25 moles) of acrylonitrile, 540 parts of 28 per cent ammonia (9 moles), 1,375 parts of water, and 1.5 parts of diphenylamine

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[1] U. S. 2,364,538 (1944).
[2] U. S. 2,335,605 (1943).
[3] U. S. 2,335,653 (1943).
[4] U. S. 2,336,067 (1943).

(as stabilizer) are heated in an autoclave for 8 hr. at 150°.[1] The resultant solution is filtered, treated with decolorizing carbon at 70°, and again filtered. The filtrate is evaporated to a thick sirupy consistency and then dissolved in 100 cc. of methanol, whereupon 39 parts of β-aminopropionic acid crystallizes out. Although the primary yield is only 35 per cent, this can be increased by treating the filtrates with aqueous ammonia and working up the product as before.

When methyl acrylate is treated as above, amination and hydrolysis also occur.[2] If the resultant sirup is extracted with a mixture of methanol and acetone, 3:1, and the solution permitted to stand at approximately 5°C. for 12 hr., the β-alanine settles out. It is then filtered and air dried. The yield of β-alanine is 68 per cent.

Preparation of Urea.—The commercial production of urea from carbon dioxide and ammonia is carried out as a continuous process (Fig. 18).[3] Approximately 102 parts of ammonia and 44 parts of carbon dioxide are compressed and delivered separately as liquids (or compressed gases) into a steam-heated autoclave at 190°C. maintaining an internal autoclave pressure of approximately 200 atmos. About 2 hr. is required for the passage of the materials through the autoclave, during which interval the reactants are almost wholly converted to ammonium carbamate, which in turn is converted largely to urea. From the autoclave, the melt, consisting of 11.7 parts of ammonium carbamate, 51 parts of urea, 68 parts of ammonia, and 15.3 parts of water, is cooled to approximately 150°C. and is then admitted to a urea still which is maintained at 60°C. Here 42.3 parts of unconverted ammonia and any unreacted carbon dioxide are removed and collected for return to the system. The urea-water solution is then delivered to a crystallizer maintained at approximately 15°C. where 18 parts of the remaining free ammonia is removed by a suitable suction pump compressor. The resultant magma is passed to a continuous centrifuge whereby 30 parts of crystalline urea are obtained. The mother liquor, comprising 11.7 parts of ammonium carbamate, 21 parts of urea, 7.7 parts of ammonia, and 15.3 parts of water, may be variously used in the manufacture of mixed fertilizer.

Materials of Construction.—Since the synthesis is carried out at elevated temperatures and at pressures from 150 to 300 atmos., it is necessary to construct the autoclave to withstand these pressures. Steel pumps of the hydraulic type are used successfully to pump liquid ammonia and liquid carbon dioxide separately into the autoclaves. The liquid in the autoclave, consisting of a mixture of urea, water, ammonium carbamate, and free ammonia, is, however, highly corrosive to ordinary materials of construction at elevated temperatures.[1] Ordinary iron and steel are rapidly dissolved in it, and chromium steel and many other alloys are rapidly attacked. Lead and silver are two of the most resistant materials, and these metals are employed as linings for the autoclave and stills used in the process. Resistant steel alloys are used in construction of the parts where lower temperatures are encountered.

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[1] Carlson and Hotchkiss, U. S. 2,377,401 (1945).

[2] Babcock and Baker, U. S. 2,376,334 (1945).

[3] DeRopp and Hetherington, U. S. 2,017,588 (1935).

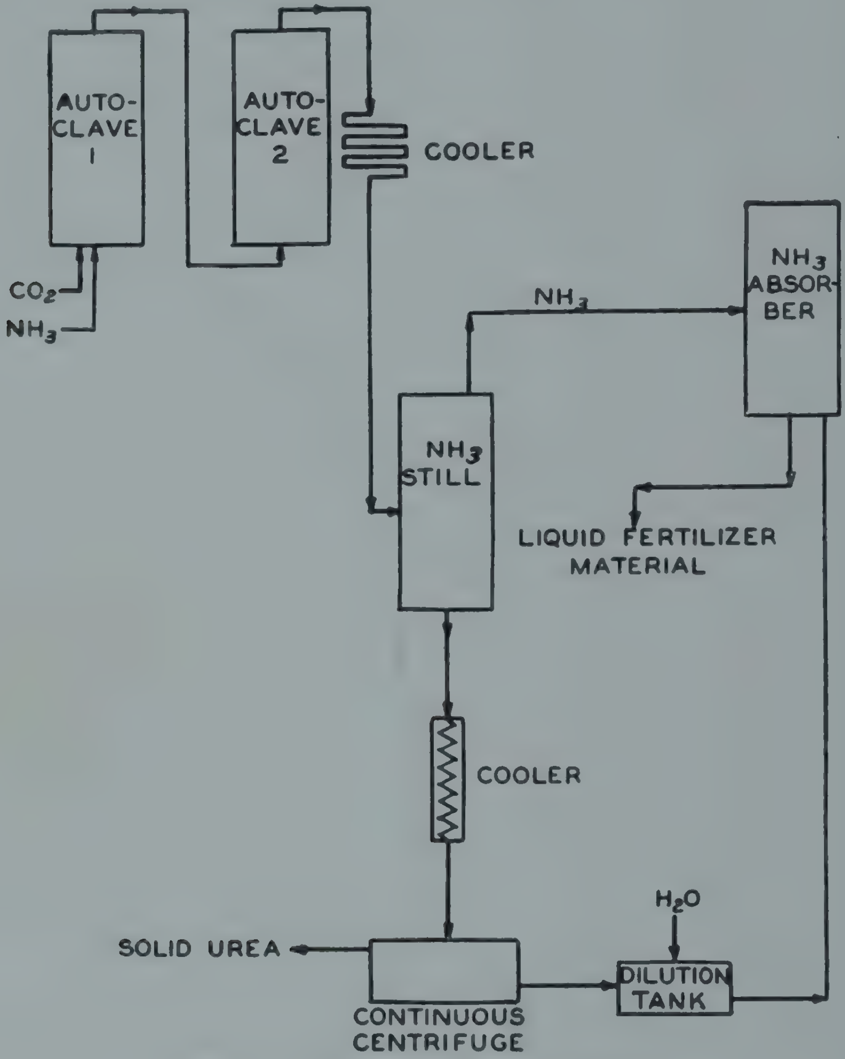
AUTO-CLAVE 1
AUTO-CLAVE 2
COOLER
CO_2
NH_3
NH_3
NH_3 ABSORBER
NH_3 STILL
LIQUID FERTILIZER MATERIAL
COOLER
H_2O
SOLID UREA
DILUTION TANK
CONTINUOUS CENTRIFUGE

FIG. 18.—Flow diagram; urea synthesis.

Preparation of Guanidine Nitrate.—Previously, it was indicated that the reaction of dicyandiamide with ammonia leads principally to melamine unless an ammonium salt is introduced as a coreactant so as to bind the guanidine which is formed initially as a stable salt. Based on these observations the technical preparation of guanidine nitrate is carried out by dissolving 10.8 parts by weight of recrystallized dicyandiamide and 20.4 parts of ammonium nitrate in 19.2 parts of liquid ammonia.[1] The mixture is charged into an autoclave fabricated from stabilized 18:8 chrome-nickel steel and equipped with internal heating coils and an agitator.

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[1] THOMPSON, KRASE, and CLARK, *Ind. Eng. Chem.*, **22**, 735 (1930).

The autoclave is heated by pumping a liquid mixture of diphenyl and diphenyl oxide (Dowtherm) at 180°C. through the coils, and a reaction temperature of 180°C. is maintained for ½ hr. The autoclave is then cooled and discharged, and the ammonia is evaporated.

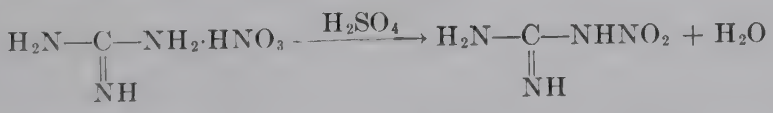
The resultant product comprises 29.9 parts of crude guanidine nitrate of 90.0 per cent purity, corresponding to a yield of 86.0 per cent. The solid product contains about 4.9 per cent of ammonium nitrate and no unreacted dicyandiamide.

The influence of varying ratios of solid reactants to NH_3 is presented in Table XIII. In these runs, the autoclave charge was discharged directly into warm water, and clear solutions were obtained. On cooling, guanidine nitrate (GN) crystallized out as a practically pure salt. When a 2:1 molar ratio of ammonium nitrate to dicyandiamide is used in conjunction with 13 moles of NH_3, high yields of a relatively pure product are obtained.

TABLE XIII.—PREPARATION OF GUANIDINE NITRATE

Dicy.	NH_4NO_3	Molar ratio	NH_3	Time, hr.	Temp., °C.	% GN in soln.	Weight solid	% GN in solid	Total % yield	% Dicy. unchanged
168	320	2:1	450	1	140	8.41	51	99.5	53.5	38.0
168	320	2:1	450	3	140	9.92	198	99.3	91.2	2.7
168	320	2:1	900	3	140	9.0	105	99.04	67.4	22.6
168	480	3:1	450	1	160	6.6	305	98.54	95.2	1.8

When guanidine nitrate is treated with concentrated sulfuric acid, the elements of water are removed and nitroguanidine is formed.



$$H_2N-\underset{\underset{NH}{\|}}{C}-NH_2\cdot HNO_3 \xrightarrow{H_2SO_4} H_2N-\underset{\underset{NH}{\|}}{C}-NHNO_2 + H_2O$$

Guanidine can readily be obtained from its salts by suspending the latter in liquid ammonia and gradually adding two molar equivalents of finely divided caustic soda to the stirred mixture. Stirring is continued for about ½ hr., during which period the insoluble inorganic salt is precipitated and removed by filtration.[2] On evaporation of the ammonia solution, a high yield of relatively pure guanidine is obtained.

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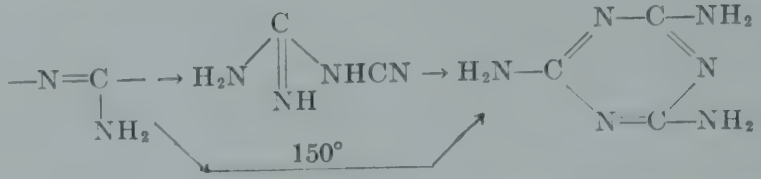
[1] U. S. 2,252,400 (1941).

[2] Thurston, U. S. 2,334,151 (1943).

Preparation of Melamine from Cyanamide.—Free cyanamide, which is obtained as colorless to pale-yellow needles, when heated to 150°, polymerizes with explosive violence to melamine or 2, 4, 6-triamino-1, 3, 5-triazine.



In practice, the polymerization of cyanamide to melamine is a stepwise process wherein the dimer (dicyandiamide) is first formed in the presence of ammonia or alkali. Conversion to the trimer (melamine) is then accomplished by heating under pressure with ammonia, preferably in the presence of a solvent such as methanol or butanol.

Pinck and Hetherington showed that the maximum conversion of cyanamide to dicyandiamide is obtained in aqueous solutions containing at least 20 per cent cyanamide.[1] The data in Table XIV represents results obtained by vigorous digestion of the reaction mass and spontaneous evaporation of the ammonia.

TABLE XIV.—POLYMERIZATION OF CYANAMIDE SOLUTIONS WITH VARYING CONCENTRATIONS OF CYANAMIDE AND AMMONIA

Conc. of initial solution		Analysis of product			
Cyanamide, %	NH_3, %	Total N, gm.	Ammonia N, gm.	Dicyanodiamide N, gm.	Conversion, %
38.0	2.4	1.294	0.004	1.228	95.2
38.0	3.6	1.216	0.006	1.154	95.3
21.7	2.4	0.708	0.003	0.680	96.6
21.7	3.6	0.640	0.003	0.625	98.2
10.0	2.4	0.365	0.004	0.110	30.6
10.0	3.6	0.435	0.006	0.212	49.4

The industrial manufacturing process consists essentially of three main steps: (1) preparation of the free cyanamide solution, by the extraction of commercial calcium cyanamide; (2) the polymerization of the solution with the formation of the relatively insoluble dicyandiamide which is removed by filtration; and (3) washing and drying of the finished product.[2]

Finely divided calcium cyanamide, which is obtained by heating calcium carbide containing an excess of lime in an atmosphere of nitrogen in an electric furnace, is mixed with water to form a slurry. The calcium is precipitated immediately with sulfuric acid or preferably with carbon dioxide, the utmost care being taken to control the temperature and pH of the extraction system. The extraction process is accompanied by a considerable temperature rise which, under appropriate pH conditions, is conducive to hydrolysis and polymerization. Any polymer formed, over and above that necessary to saturate the solution, will be lost in the calcium carbonate filter cake. With suitable carbonating apparatus, it is not difficult to keep the pH below 6.5 and above 5.7, within which limits an aqueous solution of cyanamide is relatively stable. Above pH 7, polymerization proceeds slowly, and it proceeds rapidly at a pH of 8.5.

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[1] PINCK and HETHERINGTON, *Ind. Eng. Chem.*, **27**, 834 (1935).

[2] BAUGHEN, *Can. Chem. Process Ind.*, **28**, 805 (1944).

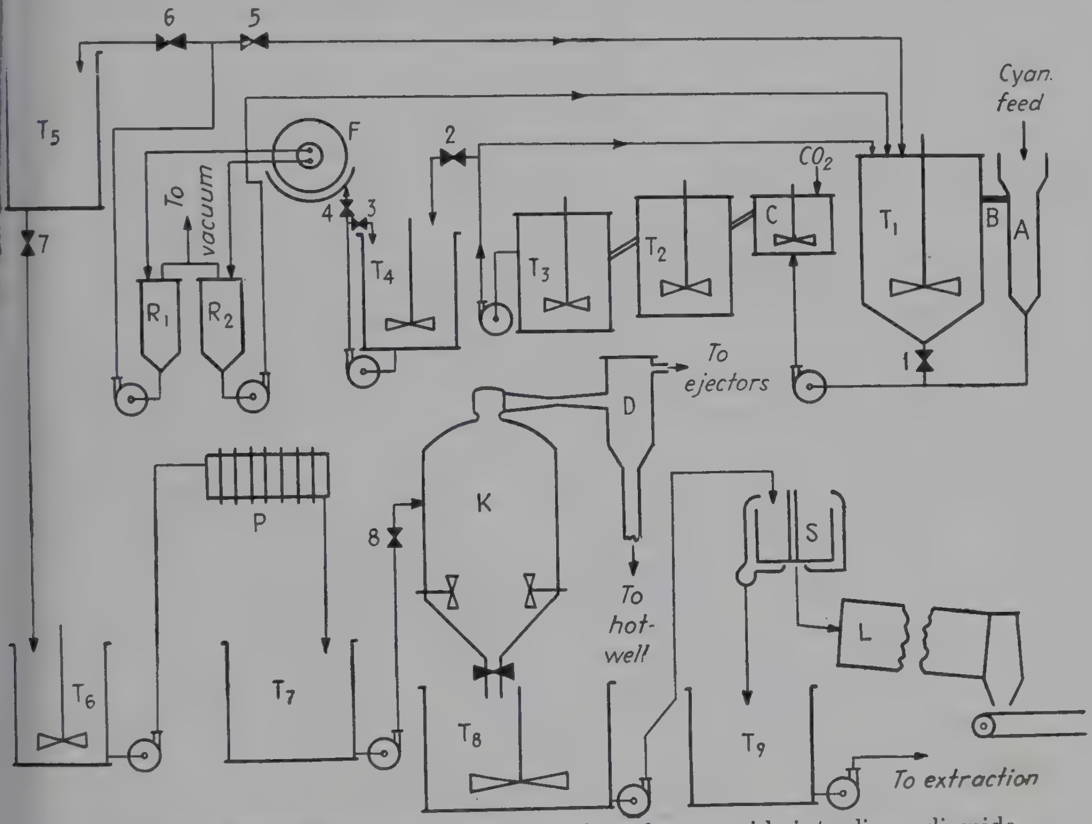

FIG. 19.—Flow diagram for the polymerization of cyanamide into dicyandiamide.

T_1 is the main slurry tank that is equipped with cooling coils. A is a standpipe into which the raw material is fed, while B is an overflow pipe through which slurry overflows continuously from T_1 to A. C is the carbonator, while T_2 and T_3 are cooling tanks equipped with cooling coils and serve to give capacity to the system. The slurry overflows from C to T_2 to T_3 and thence into a large cen- trifugal pump, which returns it to T_1. Slurry to be filtered is drawn off through valve (2) into the filter feed tank T_4, from which it is pumped to the pan of the filter F. The filter cake falls into a repulper (not shown) where it is reslurried with water and pumped either to neutralization or to waste. The strong filtrate and wash liquors collect in separate receivers R_1 and R_2, respectively. The wash liquor is returned to T_1 as shown, while the strong filtrate, if it is up to strength (20 per cent nitrogen) is divided into two parts as desired by adjusting valves (5) and (6). One portion returns to the main slurry tank T_1, while the remainder goes forward to strong-liquor storage T_5, where it is collected ready for polymerization. T_6 is a conversion tank, P the filter press, and T_7 the clear-liquor tank in which the clarified liquor is collected. K is the crystallizer and D the barometric condenser. The crystal magma is drained into tank T_8, from which it is pumped to the centrifuge S. The mother liquor passes to the sump tank T_9, while the crystals leave the centrifuge with a moisture content of 7 to 8 per cent. This is reduced to approximately 0.5 per cent in the drum drier L.

When the suspended solids in the carbonated slurry reach 25 per cent, it is filtered continuously on a rotary filter. The cake is washed with mother liquor from a previous batch and finally with water (see Fig. 19). The filtrate and washings are recycled for the extraction of more cyanamide. The precipitate, which consists chiefly of calcium carbonate and graphite, may be disposed of as waste or employed to neutralize spent acids, and the liberated carbon dioxide is employed in the carbonating operation. As soon as the filtrate contains 20 per cent nitrogen (30 per cent cyanamide), part of it is drawn off for polymerization, the volume being made up with wash water from the filters and mother liquor from the subsequent separation of dicyandiamide. The extraction operation is thus made continuous, an even balance being maintained between concentrated cyanamide liquor removed and calcium cyanamide introduced.

The polymerization, which is a batch operation, is carried out in vessels equipped with temperature-control instruments and coils through which steam or cooling water can be passed. The 20 per cent cyanamide solution is introduced, and the pH adjusted at 8.5. The temperature is then brought up to 74°C. (165°F.), and the steam shut off, the extent of the spontaneous further temperature increase being a function of the concentration of the cyanamide in solution. The reaction mass is maintained at about 80°C. (170 to 180°F.) for 2 to 3 hr., when the polymerization is practically complete. The hot liquor is then pumped through a filter press into a vacuum crystallizer.

The concentrated liquor is cooled slowly in order to obtain large crystal size and thus avoid plugging of filters. The crystal magma is pumped to a centrifuge; the mother liquor, containing a number of impurities, is largely returned for cyanamide extraction; and the crystalline dicyandiamide is delivered to a drum drier. Side reactions during the polymerization result in the formation of urea, thiourea, guanidine, melamine, ammeline, and ammelide. Although the total combined amount of these substances is not great, it is necessary to discard some of the mother liquor periodically in order to avoid operating difficulties, such as plugging of filter cloths.

Melamine is formed when dicyandiamide is heated in an autoclave with liquid ammonia. A large number of modifications of the simple procedure have been developed with the object of effecting economies in the quantity of liquid ammonia used,[1] increasing the yield and purity of the product,[2] and reducing operating difficulties.[3]

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[1] Brookes, U. S. 2,287,597 (1942); Jayne and Day, U. S. 2,341,180 (1944).

[2] Thurston, U. S. 2,223,333 (1940); Widmer, U. S. 2,265,215 (1941); Widmer, U. S. 2,288,964 (1942).

[3] Wintringham, U. S. 2,284,079 (1942); King, U. S. 2,301,629 (1942); Wintringham, U. S. 2,373,869 (1945).

Melamine is generally obtained by treating dicyandiamide with at least equal parts by weight of ammonia, preferably dissolved in methanol. The melamine precipitates out of solution and, when filtered and washed, gives a product of 95 to 96 per cent purity. Owing to the presence of comparatively small quantities of intermediate products of conversion, such as guanidine, biguanide, and guanylurea, this product is generally recrystallized for use in the preparation of resins. Furthermore, some of these impurities may react or decompose during the process and give rise to the formation of carbonates which attack the walls of the chrome-nickel-steel-alloy autoclave. This corrosive action is evidenced by the presence of iron in the recycled ammonia-methanol solution. These difficulties can be ameliorated by carrying out the preparation of melamine in a system shown diagrammatically in Fig. 20.[1]

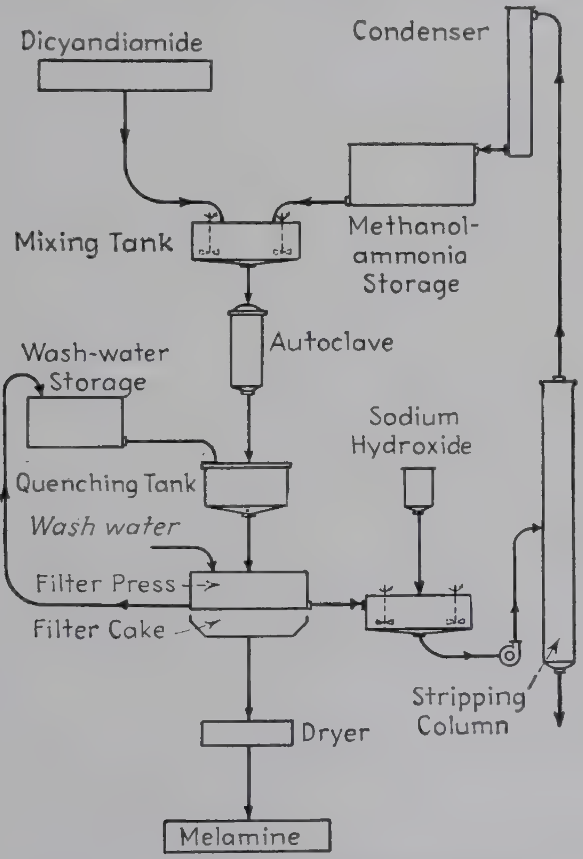
Dicyandiamide
Condenser
Mixing Tank
Methanol-ammonia Storage
Autoclave
Wash-water Storage
Sodium Hydroxide
Quenching Tank
Wash water
Filter Press
Filter Cake
Stripping Column
Dryer
Melamine

FIG. 20.—Flow sheet; preparation of melamine.

Dicyandiamide, 150 parts by weight, is dissolved in 270 parts of a water-free ammonia-methanol solution (54 per cent NH_3) contained in a mixing tank. The charge is pumped to an autoclave which is provided with a stirrer and is fabricated from chrome-nickel-steel alloy. The reactants are then heated at 180 to 200° for 2 hr. at a pressure of

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[1] Wintringham, U. S. 2,373,869 (1945).

1,600 to 1,900 lb. per sq. in. The melamine, which is present as a slurry, is discharged at about 800 lb. per sq. in. to a quenching tank containing 600 parts of wash water and 1 part of a polyhydric alcohol, such as mannitol, to prevent precipitation of iron.[1] The suspension in the quenching tank is agitated and cooled to about 50°C. by recirculating through a cooler, thus reducing solubility losses of melamine while retaining dicyandiamide and guanidine in solution. The slurry is then delivered to a filter, the mother liquor going to a closed vessel where 5 parts by weight of 100 per cent sodium hydroxide is added to each batch leaving the quenching tank. The strong alkali decomposes the volatile carbonates, with a resulting diminution of carbonate content in the recycled ammonia-methanol solution from approximately 90 to 40 parts per million. The alkali-treated mother liquor is then passed through a steam-heated stripping column in which vapors of ammonia and methanol are separated from the aqueous solution containing sodium carbonate. The ammonia-methanol vapors are condensed and returned to a storage for reuse.

The melamine on the filter is washed with about 600 parts of water, which is then placed in the quenching tank to receive the next batch of melamine from the autoclave. The product is then dried in trays at 100°, and the white, resultant material analyzes closely 95.3 per cent melamine, 0.6 per cent dicyandiamide, and 4.1 per cent cold-water insolubles.

XI. CONTROL OF THE AMMONIA-RECOVERY SYSTEM

The successful industrial preparation of amines by the ammonolysis of aromatic halides, phenols, and sulfonic acids depends largely upon the proper functioning of the ammonia system. This matter derives its importance from the fact that 5 to 15 moles of NH_3 is employed per mole of organic compound undergoing treatment. A large capital investment is, therefore, involved. It is essential, furthermore, that the excess of the ammonia be recovered and delivered to the reaction system at a constant and optimum strength. This is absolutely necessary to ensure a maximum conversion to amine of uniform quality. In properly conducted operations, the recovery is efficiently and almost automatically carried out. This is accomplished by the choice of suitable equipment and the installation of mechanically controlled devices.

The type of apparatus that may be used for the recovery of the excess of ammonia may be varied within wide limits. The physical properties of the amine and the compound from which it is derived, along with the means utilized to effect the separation of the amine, are the principal guides in the selection of the proper apparatus.

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[1] U. S. 2,324,450 (1943).

Absorption Systems.—When anhydrous ammonia is used, the essentials of a refrigeration assembly will serve for the recovery of the excess ammonia (Fig. 21). In recent years, the use of liquid ammonia, frequently in conjunction with an organic solvent, has increased markedly, and the use of high-pressure ammonia-recovery systems is destined to become more prevalent.

In liquid-phase ammonolysis with aqueous ammonia, the ammonia-recovery system may consist of a number of submerged coils, or double-pipe condensers, followed by a series of vertical absorbers. The submerged coils are cooled by circulating water, and the temperature of the vapors is brought down to 60 to 80°C. This practice makes it possible to condense and recover, in a preliminary separator tank, the weak liquor, which is then returned continuously by gravity flow to the still, while the free ammonia travels forward to effect the concentration of the liquor in the following vertical absorbers.

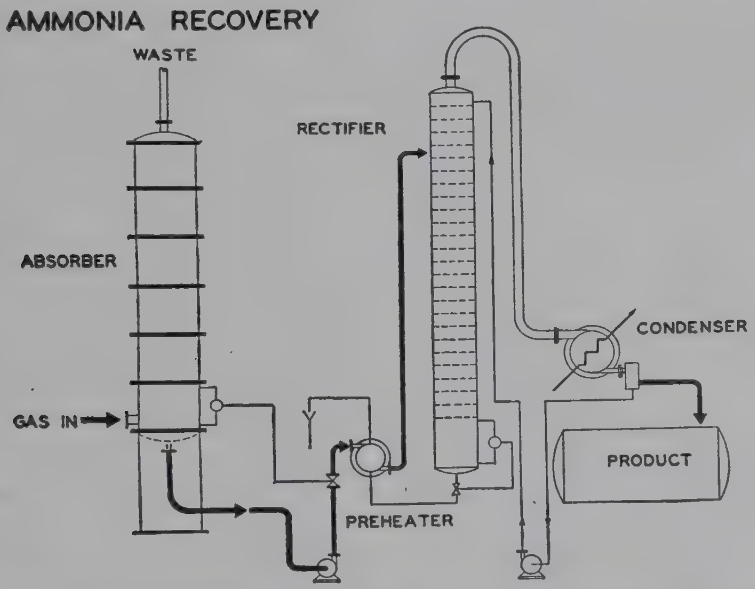


Fig. 21.—Ammonia-recovery system. Absorbers operate at atmospheric pressure. Rectifiers operate at approximately 200 lb. per sq. in.

The vertical absorbers contain aqueous ammonia of varying concentrations, and a standpipe suspended from the top supplies the NH_3 gas, which is distributed at the base by means of suitable perforated fittings. Any unabsorbed gas escapes at the top and is then led to the bottom of the following absorber. The heat of solution is removed either by internal cooling coils or by an outside spray system.

The absorbers are set on a heavy foundation of masonry, at a sufficiently high level to permit bottom connections for cleaning and transfers incidental to operations. The piping can be so arranged that the ammonia vapor is led to the absorber containing the strongest solution and then made to pass into absorbers containing liquor of progressively decreasing strength. When a sufficient number of absorbers are employed, the ammonia vapors are led in a direct manner through the absorbers. In properly conducted systems, practically no ammonia gas escapes at the exhaust from the final absorber. The efficiency in recovery should be at least 90 per cent of that theoretically possible.

The absorption tanks may be arranged in a tier so that there is a constant overflow of liquid from the final absorber, which contains almost pure water, to the lowest tank, which holds the most concentrated liquor. A pump removes the strong solution, which should be ready for reuse, to a storage tank where it is cooled prior to delivery to the pressure system.

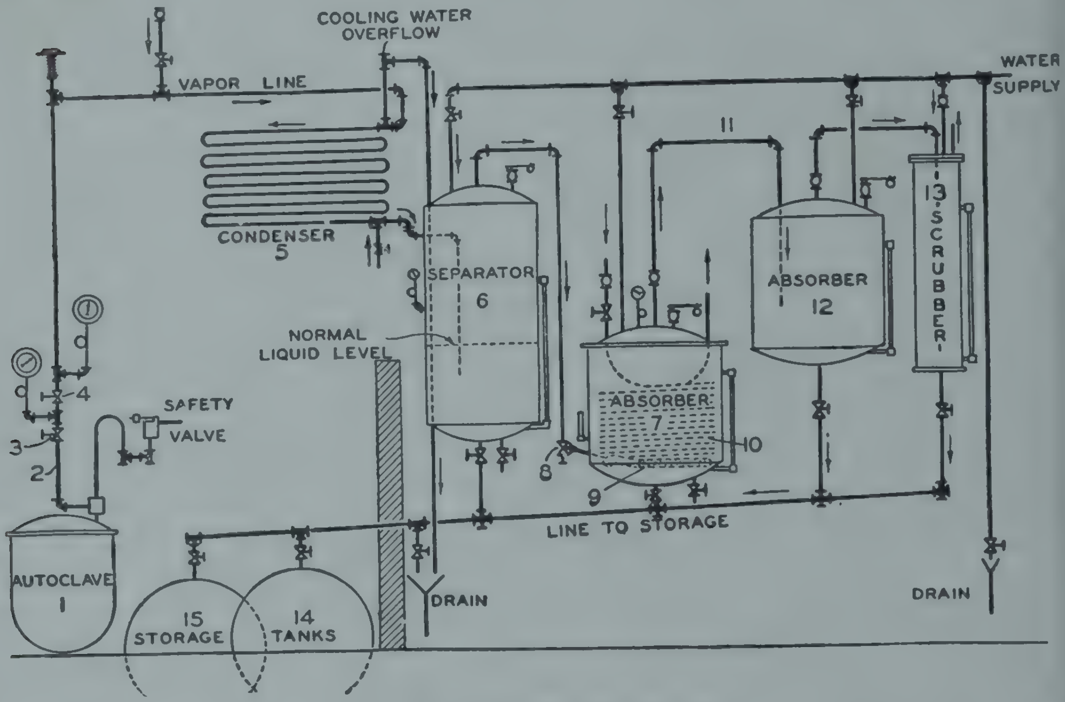

COOLING WATER
OVERFLOW
VAPOR LINE
WATER
SUPPLY
11
CONDENSER
5
SEPARATOR
6
NORMAL
LIQUID LEVEL
ABSORBER
12
13 SCRUBBER
ABSORBER
7
10
8
9
4
3
2
SAFETY
VALVE
LINE TO STORAGE
AUTOCLAVE
1
15
STORAGE
14
TANKS
DRAIN
DRAIN

Fig. 22.—NH_3 recovery system.

Description of Recovery System.—In the preparation of 2-aminoanthraquinone, the excess of ammonia may be recovered in the following manner (Fig. 22):[1] At the end of the reaction, the gaseous constituents of the reaction mixture are gradually released through line 2 by means of the needle valves 3, 4 and allowed to expand to a pressure of about 50 lb. per sq. in. The expansion causes a considerable drop in temperature, and heat is eliminated as the gaseous products flow through the cooling coil 5, resulting in a concentrated ammonia condensate. The condensate remains substantially in the separator 6. The partly dehydrated gases pass from the separator 6 to the first solution tank or

[1] U. S. 1,832,485 (1931).

absorber 7 and are further expanded to a pressure of about 5 lb. per sq. in. in their passage through the needle valve 8, thus being further cooled. Sufficient pressure is maintained on the gases to give a desired velocity and an injector action in the first solution tank, or absorber 7, which is preferably charged with a measured quantity of water or dilute aqueous ammonia. The weak liquor or water is drawn by the injector through the pipe 9, in contact with the ammonia in the gases, and the ammonia-water mixture is diffused into the balance of the ammoniacal solution. The ammonia absorption releases heat, which is removed by the cooling coil 10, a sufficient amount of cooling medium being circulated through the coil to maintain a desired temperature commensurate with the concentration of aqueous ammonia that is desired; thus, a temperature of 35°C. or thereabouts, with a proper charge of water and a pressure of the entering ammonia of about 5 lb. per sq. in., gives an aqueous ammonia of about 28 per cent concentration. Unabsorbed gases pass through line 11 into the second solution tank, or absorber 12, which is nominally at atmospheric pressure, and what gas escapes from this tank passes through the liquid in the tower 13 and out of the vent.

A number of modifications of the preceding system have given eminently satisfactory service in practical operations on a large scale. Generally, it is not advisable to release all the pressure from the autoclave. If all but 150 to 200 lb. pressure is allowed to escape, it is possible then to blow the charge under its own pressure to a vessel of lighter construction in which the amino compound undergoes subsequent treatment. The receiving vessel (still) may be prepared with an alkaline solution to decompose the combined ammonia. In this vessel, the residual ammonia is effectively removed by distillation, and the ammoniacal vapors are led to the recovery system. The residual amino compound can then be treated in any desired manner most advantageously to effect its removal:

CHAPTER VII

OXIDATION

By L. F. Marek

I. TYPES OF OXIDATIVE REACTIONS

In the organic chemical industry, oxidation constitutes one of the most powerful tools used in the synthesis of chemical compounds. The oxidation processes are many and varied and are manifested in a variety of net effects. The principal types of oxidative reactions may be set forth as follows:

1. **Dehydrogenation** is illustrated in the transformation of a primary alcohol to an aldehyde:

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$$

or a secondary alcohol to a ketone:

$$CH_3{\cdot}CHOH{\cdot}CH_3 + \tfrac{1}{2}O_2 \rightarrow CH_3{\cdot}CO{\cdot}CH_3 + H_2O$$

2. **An atom of oxygen may be introduced** into a molecule, as is illustrated by the oxidation of an aldehyde to an acid:

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH$$

or of a hydrocarbon to an alcohol:

$$(C_6H_5)_3CH + \tfrac{1}{2}O_2 \rightarrow (C_6H_5)_3COH$$

3. **A combination of dehydrogenation and introduction of oxygen** may occur, as in the preparation of aldehydes from hydrocarbons:

$$CH_4 + O_2 \rightarrow CH_2O + H_2O$$

or the preparation of benzoic acid from benzyl alcohol:

$$C_6H_5{\cdot}CH_2OH + O_2 \rightarrow C_6H_5{\cdot}COOH + H_2O$$

4. **Dehydrogenation may also be accompanied by molecular condensation,** as is the case when 2 molecules of benzene form diphenyl or 2 molecules of toluene form stilbene or when methylanthraquinone is converted to anthracene yellow C.

$$2C_6H_6 + \tfrac{1}{2}O_2 \rightarrow C_6H_5{-}C_6H_5 + H_2O$$
$$2C_6H_5{\cdot}CH_3 + \tfrac{1}{2}O_2 \rightarrow C_6H_5{\cdot}CH{=}CH{\cdot}C_6H_5 + H_2O$$

5. **Dehydrogenation, oxygen introduction, and destruction of carbon linkages** may all occur in the same process of oxidation, *e.g.*, in the oxidation of naphthalene to phthalic anhydride:

$$C_{10}H_8 + 4.5O_2 \rightarrow C_8H_4O_3 + 2H_2O + 2CO_2$$

6. **Oxidation** may be accomplished indirectly through the use of intermediate reactions:

$$C_6H_5{\cdot}CH_3 \rightarrow C_6H_5{\cdot}CCl_3 \xrightarrow{H_2O} C_6H_5{\cdot}COOH$$

$$C_6H_6 \rightarrow C_6H_5{\cdot}SO_3H \xrightarrow{NaOH} C_6H_5OH$$

$$CH_3OH + CO \rightarrow CH_3COOH$$

7. **Olefins may be oxidized** under mild conditions to hydroxy derivatives and may be converted to aldehydes and carboxylic acids of lower molecular weight when stronger oxidizers are employed. Thus, oleic acid can be converted to dihydroxystearic acid with alkaline potassium permanganate:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[\text{Alkali}]{KMnO_4} CH_3(CH_2)_7CHOH{-}CHOH(CH_2)_7{-}COOH$$

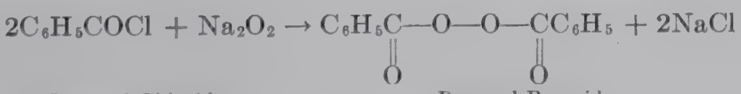
When sodium dichromate in acid solution is employed, fission as well as oxidation occur and pelargonic and azelaic acids are produced:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \begin{array}{l} \nearrow CH_3{-}(CH_2)_7{-}COOH \\ \searrow HOOC{-}(CH_2)_7{-}COOH \end{array}$$

8. **Peroxidation** occurs readily under certain conditions. Thus, some reactions occur directly with air when catalyzed by ultraviolet irradiation:

$$\text{Isopropylbenzene} \xrightarrow[\text{UV}]{\text{air}} \text{isopropylbenzene peroxide}$$

Others require the interaction of an inorganic peroxide:



$$2C_6H_5COCl + Na_2O_2 \rightarrow C_6H_5\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}C_6H_5 + 2NaCl$$

Benzoyl Chloride Benzoyl Peroxide

9. **Amino compounds** may be oxidized to azobenzene, *p*-amino-phenol, or nitrobenzene under moderate conditions, or the N-containing radical may be completely removed under drastic conditions. In this way, quinone is derived from aniline.

10. **Sulfur compounds** may be oxidized by acid permanganate, as in the preparation of sulfonals, trionals, and tetranals from $(CH_3)_2C(S{\cdot}C_2H_5)_2$ or $(CH_3)(C_2H_5)C(S{\cdot}C_2H_5)_2$ or $(C_2H_5)_2C(S{\cdot}C_2H_5)_2$, in which the sulfide

sulfur is oxidized to sulfonic groups. It should be noted that the mercaptans behave differently toward oxidizing agents from the alcohols, in that the action of strong oxidizing agents increases the valence of the sulfur atom instead of removing hydrogen, as in the case of the alcohols. Thus:

$$\underset{\text{Ethyl Alcohol}}{CH_3CH_2OH} \xrightarrow{\text{Oxidation}} CH_3CHO + H_2O$$

$$\underset{\text{Ethyl Mercaptan}}{CH_3CH_2SH} \rightarrow \underset{\text{Ethanesulfonic Acid}}{CH_3CH_2SO_2OH}$$

On the other hand, mild oxidation of mercaptans may result in the formation of disulfides. Thus:

$$\underset{\text{Ethyl Mercaptan}}{2CH_3CH_2SH} \xrightarrow{\text{Oxidation}} \underset{\text{Diethyl Disulfide}}{C_2H_5S{-}SC_2H_5} + H_2O$$

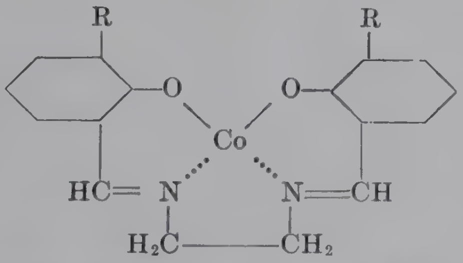
Oxidation reactions, such as those enumerated above, are accompanied by the formation of water, carbon oxides, or both or by the introduction of elemental oxygen in the organic molecule or by the step down of an oxidizing compound from an unstable state of high oxidation to a more stable state of lower oxidation. These reactions are exothermic and accompanied by a free-energy decrease. Equilibrium, therefore, is favorable, and in practically all cases no means need be provided to force the completion of the reaction. Indeed, in the majority of cases, steps must be taken to limit the extent of the reaction and prevent complete loss of product through continued oxidation.

However favorable equilibrium may be, a useful process does not result until a favorable rate of reaction is obtained. The steps that have been taken to provide these favorable reaction rates and favorable methods of control in the case of organic oxidations have led to the great variety of oxidation processes now in use. The diversity of substances that may be subjected to oxidation processes in order to obtain more useful substances has made necessary a diversity of methods. It is the purpose of this chapter to examine some of these methods and their characteristics.

The conditions imposed in these processes are such that two definite technics are used, *viz.*, vapor-phase and liquid-phase methods. Oxidations are conducted in the liquid phase in cases where high-molecular-weight, complex, and more or less thermally unstable substances are dealt with and where the oxidizing agent is relatively nonvolatile. Temperatures are low or moderate, and the extent of oxidation may be readily controlled by (1) limiting the duration of operation; (2) controlling the temperature; and (3) limiting the amount of oxidizing agent. Oxidation may occur through the action of an oxidizing agent that becomes reduced during the operation or through the action of molecular oxygen in the presence of a catalyst. Vapor-phase oxidation reactions can be effectively applied only to readily volatile substances that are of sufficient thermal stability to resist dissociation at elevated temperatures. A further limitation exists in that the desired product must also be thermally stable and comparatively resistant to continued oxidation. Solid or vapor-phase catalysts may be employed with air or oxygen to produce the desired oxidation. The temperatures, as already implied, are usually high. Control is effected by limiting time of contact, temperature, proportion of oxygen, or type of catalyst or by combinations of these factors.

Although the use of commercially pure oxygen is only rarely required for organic oxidations by molecular oxygen, the advantages resulting from the absence of the diluent nitrogen of air in product recovery may warrant the additional cost of oxygen. Substantial developments have occurred in the mechanical method of producing oxygen by the rectification of liquid air, permitting production of gaseous oxygen at low cost in much smaller units than those now in use for commercial oxygen manufacture.

During the war, various chemical methods of oxygen production have also received attention. Among these, the method making use of substances capable of absorbing oxygen from air under one set of conditions and desorbing it under another set is of interest. The cobalt derivatives of salicylaldehyde-substituted ethylene diamine and derivatives thereof have been found capable of producing oxygen in a regenerative cycle process. A typical compound of this class, where R is H,



has a theoretical oxygen-absorbing capacity of 4.05 per cent of its own weight and, under proper conditions, can be made to absorb and desorb oxygen quite rapidly.[1]

II. OXIDIZING AGENTS

As has already been stated, the principal problem involved in oxidation reaction is the induction of the desired reaction coupled with a satisfactory control of the extent of reaction. Since this is so, a study of the processes employing oxidation would best be founded on an inspection of the materials and methods used to solve these problems.

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[1] Pfeiffer, Breith, Lübbe, and Tsumaki, *Ann.* **503**, 84 (1933); Tsumaki, *Bull. Chem. Soc. Japan*, **13**, (2), 252–266 (1938).

In the case of liquid-phase oxidations, it is possible to use either gaseous oxygen or compounds having oxidizing power. To illustrate the methods that are used, the processes will first be examined from the standpoint of the oxidizing agent, and the character of the action of each agent will be pointed out later by the use of exemplary reactions.

PERMANGANATES

The solid salts of permanganic acid are powerful oxidizing agents. Calcium permanganate induces such rapid oxidation of ethanol that inflammation may result. Aqueous solutions of the permanganates also possess powerful oxidizing properties. One of the commonest and most useful of the agents employed in organic oxidations is potassium permanganate. The potassium salt is available in the form of stable crystals, whereas the sodium salt is deliquescent; consequently, the former is almost invariably used. It functions as an oxidizing agent of different strengths in alkaline, neutral, and acid solutions.

The calcium and barium salts have been used for the oxidation of complex proteins. The calcium salt has the advantage in that it forms insoluble products. The calcium oxide combines with the manganese dioxide to form the insoluble $CaO:MnO_2$, thus simplifying recovery of products.

Alkaline Solution.—When potassium permanganate alone is used in aqueous solution, the solution becomes alkaline through the formation of potassium hydroxide:

$$K_2Mn_2O_8 + H_2O \rightarrow 2MnO_2 + 2KOH + 3O$$

Three atoms of oxygen are released per molecule of permanganate, and manganese dioxide in the hydrated form is precipitated.

In the case of acid products, the potassium salts usually form. After the removal of the MnO_2 by filtration, the acid may be recovered by acidification with a mineral acid. Very dilute aqueous solutions are used in the oxidation of toluene derivatives to the corresponding acids. Loss of color shows the end point. Excess of reagent is easily remedied by the addition of ethanol or other harmless reducing agent. Thus,[4] *p*-chlorotoluene is oxidized to *p*-chlorobenzoic acid; naphthalene to phthalonic acid; maleic acid to mesotartaric acid; *o*-nitrophenol to dinitrodihydroxydiphenyl. In general, however, hydroxy and amino groups must be protected by alkylation or acylation to prevent oxidation of the substitutent.

An excess of alkali may be added at the start, in which condition potassium permanganate is used for oxidizing ortho substituted derivatives of toluene. Thus, *o*-toluic acid yields phthalic acid. Substituted cinnamic acids are oxidized to the corresponding benzoic acids. Triphenylmethane is oxidized to the corresponding alcohol; diphenyl methane to the ketone; and oleic acid to dihydroxystearic acid.

Neutral Solution.—To avoid the alkalinity produced by the use of potassium permanganate alone as an oxidizing agent, resort may be had to the introduction of carbon dioxide to neutralize the alkali or to the use of magnesium sulfate for the formation of neutral potassium sulfate and insoluble magnesium oxide. These expedients are necessary in very few cases, however.

In such a neutralized oxidizing solution, acet-*o*-toluidide gives a yield of 80 per cent of the oxidation product acetanthranilic acid; whereas in the alkaline solution, a yield of only about 30 per cent is obtainable.

Acid Solution.—The addition of acetic or sulfuric acid to potassium permanganate solutions yields a powerful oxidizing agent useful only in the preparation of very stable compounds. The powerful action of this agent markedly restricts its applicability. In use, the oxidizing solution is added gradually to the substance undergoing oxidation, since in this way the action is limited and controllable. Each moleucle of permanganate yields 5 atoms of oxygen.

$$K_2Mn_2O_8 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$$

Acid solutions may be used for the preparation of certain naphthalenesulfonic acids incapable of formation by other means. Both aliphatic and aromatic sulfides or hydro sulfides are oxidized to corresponding sulfonic acids. *o*-Iodobenzoic acid is oxidized to *o*-iodosobenzoic acid.

DICHROMATES

The usual form of oxidation with dichromates is in the presence of sulfuric acid and with the sodium or potassium salt. Although the dichromates exert an oxidizing tendency in the absence of acid, the oxidation reaction can be made to occur much more quickly in the presence of acid, and acid solutions are almost invariably used. Such mixtures react to give oxygen as follows:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

2 moles of chromic acid (1 mole of dichromate) giving 3 atoms of oxygen. The sodium salt is the cheaper, is much more soluble in water, and is consequently more often used.

Chromic Acid Solution.—Chromic anhydride (CrO_3), dissolved in glacial acetic acid, is sometimes used as an oxidizing agent. Two moles of the anhydride yield 3 atoms of oxygen: $2CrO_3 \rightarrow Cr_2O_3 + 3O$. In practice, only the theoretical amount of the oxidizing agent is added, and this is usually introduced gradually as the oxidation proceeds. Aromatic alcohols may be oxidized to aromatic aldehydes, provided a primary amine is present to form a Schiff's base with the aldehyde as soon as it is formed. Quinoline homologues are oxidized to quinoline carboxylic acids. If acetic anhydride is used, benzene homologues may be oxidized to aldehydes, since the formation of the acetyl derivatives prevents further oxidation.

12-Hydroxy-stearic acid, derived from ricinoleic acid from castor oil, may be oxidized with chromic acid (CrO_3) dissolved in acetic acid to form 12-ketostearic acid. The esters of this keto acid are useful stabilizers and plasticizers for lacquers, plastics, and resins.[1] Catalytic dehydrogenation in the presence of active catalysts, such as nickel-on-kieselguhr or copper-cadmium-chromite, may also be used to convert 12-hydroxystearic acid derivatives to the keto acids.[2]

Chromic acid in hot glacial acetic acid oxidizes anthracene quantitatively to anthraquinone in a very smooth reaction, but the method is too expensive for commercial application in competition with synthetic anthraquinone made from cheap phthalic anhydride and benzene by means of the Friedel-Crafts reaction. Prior to the development of the present methods of phthalic anhydride manufacture, the process was used extensively for anthraquinone production in Europe. The method has been recommended for anthracene analysis.

Chromic acid and the dichromates find numerous other applications as oxidizing agents in the organic chemical industry. In the manufacture of perfumes, they may be used to oxidize anethole to anisic aldehyde; isosafrol to piperonal (heliotropin); etc. The dichromates may be used to effect the condensation of α-naphthol with dimethyl-*p*-phenylenediamine to form indophenol. They are used in the preparation of methylene blue, safranine, and other dyestuffs.

Hypochlorous Acid and Salts

The lithium,[3] sodium, and calcium salts of hypochlorous acid are known in the solid state. Although they decompose easily when wet, they are stable if thoroughly dry. Bleaching powder, formed by reacting chlorine with dry calcium hydroxide, is related to the hypochlorites and depends upon the presence of the hypochlorite radical for its characteristic action. Chlorinated solutions of zinc and aluminum hydroxides are more active oxidizing agents than are comparably treated solutions of the alkalies or alkaline earths because of greater hydrolysis and consequent more rapid decomposition of hypochlorous acid. But the sodium salt has the advantage of ease of preparation and handling.

Hypochlorous acid is unstable and decomposes very easily to liberate oxygen. Decomposition rate is not violent, however, and for some purposes may even be increased by the use of a cobalt or nickel salt to act as a catalyst. The action of the salts, especially those of the alkalies or alkaline earths, may be increased by the addition of carbon dioxide or acids because of the more rapid liberation of the hypochlorous acid caused thereby. This property furnishes a method of control when these substances are used for oxidation.

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[1] Cox, U. S. 2,180,730 (1939).

[2] Lazier, U. S. 2,178,760 (1939).

[3] Laue, U. S. 2,384,629 (1945).

Calcium hypochlorite is used to a large extent for bleaching linen and cotton textile materials and paper pulp. The sodium salt is used in bleaching rayon yarn. Both salts are used for "sweetening" uncracked gasolines by the oxidation of the mercaptans to sulfides and disulfides.

SODIUM CHLORITE AND CHLORINE DIOXIDE

Sodium chlorite, $NaClO_2$, is marketed as an 80 per cent dry powder for use in bleaching. When reacted with chlorine, sodium chlorite releases chlorine dioxide, ClO_2, a gas at normal temperatures and soluble in water. Chlorine dioxide is a powerful oxidizing and bleaching agent; but because of its instability, it cannot be produced and stored.[1] The aqueous solutions are decomposed by light to perchloric and chloric acids, oxygen, and water.

Chlorine dioxide has been found to have utility in bleaching and maturing flour, treating water, checking blue mold in citrus fruits, and bleaching textiles.

CHLORATES

Chloric acid, $HClO_3$, is a powerful oxidizing agent. It may be obtained in aqueous solutions at concentrations up to about 40 per cent and is stable at temperatures up to 40°C. Such a solution will ignite paper immersed in it. When the oxidizing action of this agent is controlled, it is possible to effect the oxidation of ethanol or ethyl ether to acetic acid, of ethylene to glycol, of allyl alcohol to glycerine, of fumaric acid to racemic acid, etc. In conjunction with mineral acids, chloric acid oxidizes aniline to aniline black. However, since its aqueous solutions must be obtained by double decomposition from its salts, its industrial usefulness is very limited, and it is more often used in the form of the soluble salts.

Potassium chlorate is a powerful oxidizing agent. However, its solubility in water is limited, being only 3.3 gm. per 100 gm. of water at 0°C. and 56.5 gm. per 100 gm. of water at 100°C. It has been widely used in the dry, finely divided state as an oxidizing agent and in the laboratory as a source of pure oxygen. Mixed with reducing agents such as carbon, sulfur, sugar, and cellulose, it is used in the manufacture of powder, fireworks, explosives, matches, etc. In solution, it has been used in the oxidation of aniline in the production of aniline black. When heated to above its melting point (357°C.), the dry salt tends to decompose to potassium chloride and oxygen, each molecule of chlorate giving 1½ molecules of oxygen. Concurrently with the above decomposition, potassium chlorate decomposes to give the perchlorate and the chloride. The relative speed of the two reactions varies with the temperature and is markedly affected by catalysts. Thus, the decomposition to oxygen may completely outrun the other reaction in the presence of a manganese dioxide catalyst.

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[1] WOODWARD, PETROE, and VINCENT, *Am. Inst. Chem. Eng.*, **40**, 271 (1944); HUTCHINSON and DERBY, *Ind. Eng. Chem.*, **37**, 813 (1945).

The solubility of sodium chlorate in water is far greater than that of the potassium salt, being above 80 gm. per 100 gm. of water at 0°C. and above 230 gm. per 100 gm. of water at 100°C. Also, it is less expensive, and about 15,000,000 lb. of it are used annually in the United States as a herbicide. Crotonaldehyde is oxidized to alpha methyl glycerol by reaction with sodium chlorate in the presence of small proportions of osmic acid.[1]

PEROXIDES

The principal peroxides used as oxidizing agents are those of lead, manganese, and hydrogen.

PbO_2.—Lead peroxide is used as an oxidizing agent in conjunction with acetic, sulfuric, or hydrochloric acids, usually the first. One mole yields 1 atom of oxygen, and a salt of the acid is formed during the process. It must be used in a finely divided form and, for this reason, is best prepared by precipitation from a solution of lead nitrate by the addition of sodium hypochlorite or bleaching powder.

MnO_2.—Manganese dioxide is widely used as an oxidizing agent in both its natural and prepared forms. It is employed in conjunction with sulfuric acid and during the reaction is reduced to manganese sulfate, releasing 1 atom of oxygen per mole. One of its principal uses is in the oxidation of methyl groups to aldehyde groups, in which role it has been largely used to convert toluene to benzaldehyde.

H_2O_2.—Hydrogen peroxide is manfactured, marketed, and used as an aqueous solution, the strength of which is customarily designated in terms of the volume of free oxygen equivalent. Thus, the most widely used concentration is "100-volume peroxide," from which 100 volumes of oxygen per volume of solution may be obtained. Practically all hydrogen peroxide is manufactured electrolytically by two processes, one using persulfuric acid and the other ammonium persulfate. A small proportion s manufactured from barium peroxide.[1]

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[1] Staudinger and Tuerck, U. S. 2,351,302 (1944).

Although hydrogen peroxide is generally marketed industrially as the 100-volume product (31.3 gm. H_2O_2 per 100 cc. solution, or 28.5 per cent H_2O_2 by weight) in glass carboys, aluminum drums, and aluminum tank cars, some 130-volume material is shipped in tank cars where long hauls make the freight saving an advantage. The best organic stabilizers are the antipyretic drugs such as acetanilide, salicylic acid, aspirin, phenacetin, and antipyrine, which are used in amounts of 0.01 per cent or less. It is possible to make stronger solutions than these, but they have no present industrial importance.

The bulk of the hydrogen peroxide consumed industrially is used in textile bleaching, hydrogen peroxide having displaced chlorine and the hypochlorites in portions of this field because of use advantages and despite a relatively higher cost. Substantially all silk and wool goods, rayon fabrics, and cotton goods lighter than about 5 yd. per lb. are bleached by hydrogen peroxide. Also fur skins and cotton goods partly dyed or striped are usually hydrogen peroxide bleached.

Despite the decided advantage of hydrogen peroxide as an oxidizing agent because of freedom from residual salts, precipitates, gases, etc., only limited use has been made of it as an oxidant in the organic chemical industry, largely because of relatively higher costs. However, with perfection of manufacturing methods, increased production, and a wider market base, lower prices may occur and the use of hydrogen peroxide as an oxidant increase. Considerable interest has been attached to very high-strength hydrogen peroxide, approximately 80 to 85 per cent, for certain military uses, including the propulsion of rockets and submarines.[2] As one result of this interest, attention has been given to unique methods that might permit large low-cost manufacture. One such method obtains hydrogen peroxide by passing a mixture of 98 per cent hydrogen and 2 per cent oxygen at 400 to 650°C. through a reaction vessel coated with boric acid (boron oxide), the function of the boric acid coating being to retard decomposition of hydrogen peroxide produced in the combustion.[3] Instead of hydrogen, it is possible to use hydrocarbons in a similar way. Thus, hydrogen peroxide is formed by reaction of a 90 per cent propane-10 per cent oxygen mixture for 5 sec. at 470°C.[4]

A number of transformations are possible with hydrogen peroxide. In alkaline solutions, it may be used in the preparation of organic peroxides such as benzoyl peroxide and diethyl peroxide. A 3 per cent solution oxidizes piperidine to glutaric acid by rupture of the ring. Benzene yields a small amount of phenol. Phenols are converted to dihydric phenols or quinones. By the action of hydrogen peroxide in the presence of small amounts of ferrous salts, hydroxy acids are converted to aldehydo or keto acids. Very small amounts of selenium oxychloride markedly accelerate the rate of reaction of hydrogen peroxide in oxidizing aldehydes to acids. In the presence of catalysts, such as the oxides of ruthenium, vanadium, chromium, or molybdenum, hydrogen peroxide adds to unsaturated organic compounds as two hydroxyls, giving glycols.[1] The chief addition compound of commercial importance is urea hydrogen peroxide, a solid material containing 36.17 per cent hydrogen peroxide.

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[1] See SLATER, *J. Soc. Chem. Ind.*, **6**, 42–46 (1945), for a general discussion of peroxides.

[2] *Chem. Eng. News*, **23**, 1519, 1626 (1945) basis of data collected by Industrial Intelligence Staff, Chemical Warfare Service.

[3] Cook, U. S. 2,368,640; U. S. 2,368,806 (1945).

[4] Lacomble, U. S. 2,376,257 (1945).

Peroxides of the alkaline earths have limited industrial uses, the peroxides of calcium, magnesium, and zinc having pharmaceutical uses.

The principal peroxy hydrates of commerce are sodium perborate and sodium percarbonate, which are used to replace hydrogen peroxide where a dry substance is desired. Sodium perpyrophosphate has limited use as a bleaching and dyeing auxiliary.

Na_2O_2.—Sodium peroxide is used in only a limited way industrially for oxidizing organic substances, partly because of the hazards associated with its storage and use. After considerable research effort, sodium peroxide is being utilized in the commercial production of bleached groundwood pulp.[2]

By the action of sodium peroxide, phenanthraquinone in aqueous suspension changes smoothly to diphenic acid (biphenyl-2, 2′-dicarboxylic acid). By the action of a cooled solution of sodium peroxide on the acid chloride, it is possible to form benzoyl peroxide ($C_6H_5{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}C_6H_5$).

SeO_2.—Selenium dioxide presents some interesting features as an oxidizing agent[3]. For instance, unsaturated substances containing the grouping $—CH{=}CHCH_2—$ can be oxidized to α, β-unsaturated ketones (α pinene to verbenone);[4] substances in which a methylene or methyl group is adjacent to a carbonyl group can be oxidized so that one or more of the hydrogen atoms become oxidized (acetone to pyruvic aldehyde, acetophenone to phenylglyoxal);[5] and substances like ethanol can be made to inflame in an SeO_2 atmosphere at 230°C. (446°F.). The SeO_2 becomes reduced to selenium metal which may be easily recovered, reoxidized by heating in the presence of oxygen, and reused.

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[1] Milas, *Chem. Soc. Ann. Rept.*, **1943,** 107; Brit. 508,526.

[2] *Chem. Eng. News*, **23,** 1540 (1945).

[3] Waitkins and Clark, *Chem. Rev.*, **36,** 235–290 (1945).

[4] Schwenk and Borgwardt, *Ber.*, **65B**, 1601–1602 (1932).

[5] Riley, U. S. 1,955,890 (1934); also Astin, Newman, and Riley, *J. Chem. Soc.*, **1933,** 391–394.

Silver Oxides.—Silver has the capacity to act as an oxygen carrier or oxidation catalyst, presumably because it can form oxides other than the common Ag_2O. Although not extensively used as such, the oxide (Ag_2O) acts as a mild oxidation agent. Moist, freshly prepared silver oxide is frequently used in the organic chemical laboratory for the replacement of halogen atoms by the hydroxyl group.

Silver oxide (Ag_2O) acts as a mild oxidizing agent and oxidizes glycerol to glycolic acid; aldehydes to acids; *o*-dihydroxybenzene to *o*-benzoquinone, being reduced to metallic silver. The oxide is fairly readily reduced by hydrogen gas. Silver oxide made alkaline with sodium or ammonium hydroxide oxidizes $=CHOH$ and $=CO$ groups when these are attached to two $-CH_2OH$ or $-COOH$ groups or combinations. Thus, alkaline Ag_2O is reduced by tartaric acid, glycerol, mannitol, etc. Neutral or acid Ag_2O is reduced by glycolic, lactic, or malic acids.

Silver oxide is an excellent oxidation catalyst for vapor-phase reactions and is used commercially, notably in the oxidation of ethylene to ethylene oxide.

NITRIC ACID AND NITROGEN TETROXIDE

Nitric acid is seldom used as an oxidizing agent in the formation of partially oxidized products. The fuming acid is used in the complete oxidation of organic compounds for the estimation of halogens or sulfur in the Carius process. The principal disadvantage of nitric acid as a partial oxidizing agent arises from its tendency to act as a nitrating agent. Even when dilute solutions are used, the products of oxidation contain nitro derivatives. The method of Krafft uses the concentrated acid (sp. gr., 1.5) and is particularly effective in the partial oxidation of substances that are already nitrated. A temperature of 0 to 5°C. is used for mixing the acid and organic compound; this is gradually raised to 50°C., and the product poured into water. Dinitroxylene is oxidized in this way to dinitrophthalic acid. Oxidation with dilute acid is slow when applied to the benzene homologues. Carboxylic acids are formed. Thus, pentamethylbenzene dissolved in benzene is converted to tetramethylbenzoic acid by boiling for 60 hr. with dilute nitric acid. *o*-Xylene is oxidized by dilute, boiling nitric acid to *o*-toluic acid. Treatment with potassium permanganate is required for the oxidation of the remaining methyl group to form phthalic acid.

Oxalic acid is obtained from nitric acid oxidation of carbohydrates.[1] Succinic acid results in good yields from nitric acid oxidation of tetrahydrofuran with acid concentrations from 50 to 75 per cent and temperatures from 20 to 40°C.[2] Oxidation with nitric acid of a secondary

[1] Brooks, U. S. 2,322,915 (1943).

[2] Ebel, U. S. 2,312,468 (1943).

aliphatic alcohol or an aliphatic ketone results in fission of the aliphatic chain at the point of attachment of the functional group accompanied by oxidation to yield 2 molecules of carboxylic acid.[1] Alpha, omega dicarboxylic acids result from nitric acid oxidation of the product of polymerizing ethylene with a vinyloxy compound.[2]

The commercially inexpensiveness of nitrogen tetroxide should stimulate research in its use as an oxidation agent. Riebsomer has reviewed the literature and pointed to the need for repetition under carefully controlled conditions of much of the earlier work because of conflicting reports of results obtained by previous workers.[3] A great many substances have been oxidized by nitrogen tetroxide, including various hydrocarbons and substituted hydrocarbons. In most cases, the products were found to be complex mixtures and have not been well characterized.

NITROBENZENE

Although nitrobenzene acts as a sufficiently strong oxidizing agent to oxidize sodium methylate to sodium formate, its action is moderate enough to make it a useful agent for particular reasons. Inorganic reducing reagents such as alkaline stannous chloride reduce nitrobenzene to azobenzene. When used in the quinoline synthesis, it may become reduced to aniline.

FERRIC SALTS

Ferric chloride is a mild oxidizing agent, 2 moles of the chloride yielding the equivalent of 1 atom of oxygen in passing to the ferrous condition.

$$2FeCl_3 + H_2O \rightarrow 2FeCl_2 + 2HCl + O$$

It transforms hydroquinone to quinone, naphthol to dinaphthol, and hydroxylamine derivatives to nitroso compounds. It has been used in the formation of acridine yellow by oxidizing the leuco base obtained from condensation of *m*-toluylenediamine with formaldehyde.

With phenols, ferric chloride gives a variety of highly colored compounds. However, the reaction is of significance principally from its use in the identification of the substances in analysis.

COPPER SALTS

Copper is capable of existing in two states of oxidation and of passing readily from one to the other of these states by oxidation or reduction. In its higher state of oxidation, it is capable of acting as an oxidizing agent and, in its lower state, as a reducing agent. This property makes the metal a useful material as an oxygen carrier or oxidation catalyst. It is more frequently used in the latter capacity than in the capacity of an oxidizing agent alone in organic chemical synthesis. When used as an oxidizing agent in solution, it is generally reduced from the cupric to the cuprous state.

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[1] Olin, Fritsch, and Hinds, U. S. 2,267,377 (1941).

[2] Hanford, U. S. 2,360,673 (1944).

[3] RIEBSOMER, *Chem. Rev.*, **36**, 157–233 (1945).

Fehling's Solution.—In the determination of sugars and in their study, use is made of the relative ease of oxidation. Both aldoses and ketoses are capable of oxidation, the ketoses the more readily. Hydroxy ketones resemble aldehydes in their ease of oxidation. For oxidation, Fehling's solution is commonly used. This consists of an aqueous solution of sodium potassium tartrate, sodium hydroxide, and copper sulfate, essentially an alkaline solution of cupric hydroxide. The sugar reduces the cupric ions to the cuprous form, and red cuprous oxide is precipitated. This solution has a rather weak oxidizing power and acts only on substances that are easily oxidized. Alcohols, acids, and simple ketones are not oxidized. Aldehydes, hydroxy ketones and di- and triphenols are oxidized readily by this solution. When, for example, glucose is heated with Fehling's solution, a precipitate of cuprous oxide rapidly forms, and reaction is complete in a few minutes. Copper salts other than the sulfate may be used, and any polyhydric alcohol such as sucrose or glycerol may be employed in place of the sodium potassium tartrate. Neither sucrose nor glycol is oxidized by Fehling's solution, and either one prevents the undesired precipitation of cupric hydroxide that would normally occur in the alkaline solution. An alkaline solution is used, since oxidation is more rapid.

Copper sulfate has been used as a catalyst in the oxidation of toluene to benzaldehyde by the use of manganese dioxide and sulfuric acid. This reaction requires specific catalysts and delicate control in order to prevent oxidation to benzoic acid. The relatively easy oxidation or dehydrogenation of benzoin to the diketone benzil may be accomplished with complex cupric salts.

ALKALI FUSION

Fusion with alkali in the presence of air (oxygen) often accomplishes oxidations impossible to obtain otherwise. For instance, the formation of oxyacids from substituted phenols by direct oxidation of side chains is difficult of accomplishment because of the much greater susceptibility of the hydroxyl group to attack and consequent tendency for the breakdown of the molecule. Alkali fusion accomplishes the desired reaction but with poor yields. Xylenols yield the corresponding mono- and dibasic acids by the reaction. Thus, *p*-xylenol is successively oxidized to *m*-homosalicylic acid and to hydroxyterephthalic acid.

The alkali fusion is of importance in the formation of certain anthraquinone vat dyes. Thus, fusion of β-aminoanthraquinone with 2 or 3 parts of potassium hydroxide at 250°C. for ½ hr. yields Bohns' Indanthrene blue RS (N-dihydro-1,2:1′,2′-anthraquinoneazine). Similarly, benzanthrone yields Bally's Indanthrene dark blue BO.

A mixture of caustic soda and potassium nitrate or chlorate possesses oxidizing powers, whereas caustic soda alone acts as a condensing and dehydrating agent. A good example of the use of the oxidizing mixture is in the formation of the dye alizarin from anthraquinone-β-sulfonic acid, sodium salt.

ARSENIC ACID

Arsenic acid (H_3AsO_4) may be obtained easily by oxidizing arsenic or arsenic trioxide with nitric acid, aqua regia, or chlorine water or slowly by oxidizing with elemental oxygen in alkaline solutions. It is easily and permanently soluble in water, the anhydride As_2O_5 being unstable in solution, in contrast to the anhydride of arsenious acid, As_2O_3. It acts as an oxidizing agent, releasing 1 atom of oxygen per atom of arsenic, in passing from the pentavalent form to the trivalent form. Although arsenic acid was formerly used for various organic oxidations, its toxic nature and the difficulty of suitably recovering the trioxide have gradually caused its abandonment in favor of less objectionable agents.

POTASSIUM FERRICYANIDE

A seldom used oxidizing agent is potassium ferricyanide, which becomes reduced to the ferrocyanide during the process, 658 parts (2 moles) of the salt yielding 16 parts (1 atom) of oxygen. It is difficult to remove the reduced salt from the product, and large amounts must be used to obtain a small amount of oxidation. Nitrotoluenes are oxidized to nitrobenzoic acids; *sym*-trinitrobenzene is oxidized to picric acid; nitroso derivatives to nitro derivatives; etc.

FUMING SULFURIC ACID (OLEUM)

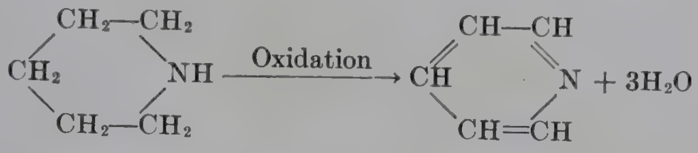
Fuming sulfuric acid ($H_2SO_4 + SO_3$) in the presence of mercury salts is a powerful oxidizing agent. It was formerly used extensively in this way for the oxidation of naphthalene to phthalic anhydride but has been displaced in this operation by the newer air-oxidation processes.

Fuming sulfuric acid attained importance as an oxidizing agent for the introduction of hydroxyl groups in anthraquinone derivatives in the production of a variety of alizarin dyes. Thus, fuming sulfuric acid at low temperatures may be used to convert alizarin and other hydroxy derivatives of anthraquinone to trihydroxy or up to hexahydroxy derivatives.

An early use of sulfuric acid as an oxidizing agent was in the oxidation of ethyl mercaptan to diethyl disulfide. However, to effect this reaction,

$$2C_2H_5SH \xrightarrow{\text{Oxidation}} C_2H_5S{-}SC_2H_5 + H_2O$$

the oxidation must be mild and controlled, since with strong oxidizing agents the sulfonic acid is formed. Also, piperidine (hexahydropyridine) may be oxidized to pyridine. The pyridine ring is very stable to oxidation, not being attacked by nitric or chromic acids and yielding a sulfonic acid only at high temperatures.



Ozone

For successful application of any ozone oxidation process, cheap electric power must be available for ozone generation. It is worthy of note, therefore, that the technically successful oxidation of isoeugenol to vanillin in Germany was abandoned because of economic reasons. Many other applications of ozone oxidation have been made or suggested, such as bleaching, sterilization of water, oxidation of acetylene to glyoxal, oxidation of anethole to anisic aldehyde, oxidation of manganates to permanganates, and drying of printing inks.

III. LIQUID-PHASE OXIDATION WITH OXIDIZING COMPOUNDS

The oxidation of aniline furnishes an example for comparison of a number of oxidizing agents. Results obtained by conducting the reaction under conditions best suited for the particular agent are shown in the following tabulation.[1]

Oxidizing Agent	Product
Manganese dioxide in sulfuric acid	Quinone
Potassium dichromate in dilute sulfuric acid at 0 to 10°C. for 24 hr.	Quinone
Potassium permanganate:	
Acid	Aniline black
Alkaline	Azobenzene plus ammonia
Neutral	Azobenzene plus nitrobenzene
Alkaline hypochlorite	Nitrobenzene
Hypochlorous acid	*p*-Aminophenol

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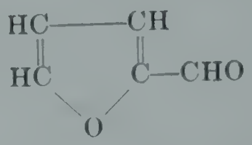
[1] Bernthsen, "Textbook of Organic Chemistry," rev. trans., p. 664, D. Van Nostrand Company, Inc., New York, 1922.

Another substance exhibiting a variety of actions toward oxidizing agents is furfural:



The aldehyde group normally behaves like that of acetaldehyde toward oxidation, but, in the presence of certain agents, the ring structure is destroyed and polybasic acids formed.[1]

Oxidizing Agent	Product
Sodium chlorate in neutral solution with V_2O_5 catalyst	Fumaric acid
Sodium chlorate in dilute acid with OsO_4 catalyst	Mesotartaric acid
Caros' acid, $HO{\cdot}O{\cdot}SO_3H$, a strong oxidizing agent	Succinic acid
Hydrogen peroxide in presence of ferrous salts	δ-Hydroxyfurfural
Bromine water at 100°C	Mucobromic acid
Potassium permanganate (diluted solution)	Pyromucic acid

The action of oxidizing agents on organic compounds depends not only upon the nature of the agent or the compound but also upon such factors as concentration, temperature, hydrogen-ion concentration, and method of mixing. Consequently, any comparison of the variety of effects obtainable by varying the oxidizing agent or organic compound cannot be pursued too far.

Ethylenic Bonds to Dihydroxy Groups.—The oxidation of olefins and olefin derivatives with dilute aqueous potassium permanganate may be used for the formation of dihydroxy compounds. Thus, oxidation of 11 liters of isobutylene with 1 per cent potassium permanganate solution results in the formation of 22 gm. of isobutylene glycol, 4 gm. of oxyisobutyric acid, and 1.5 gm. of acetone.[2] Ethylene reacts more slowly than either propylene or isobutylene[3] when treated in this way, and the isomeric diamylenes are quite unreactive, resisting oxidation for several days.[4] The rate of reaction is retarded by low temperatures and low concentrations of permanganate.[5] With 2 per cent permanganate solution, cinnamic acid yields phenyl-glyceric acid through the formation of a glycol derivative. Dilute permanganate oxidizes ethylenic bonds of fatty acids to dihydroxy groups, thus oleic acid to dihydroxystearic acid.

Hydrogen peroxide in the presence of catalysts of the oxides of Ru, V, Cr, or Mo also oxidizes organic unsaturated compounds to glycols.

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[1] Milas, *J. Am. Chem. Soc.*, **49**, 2005 (1927).

[2] Wagner, *Ber.*, **21**, 1232 (1888).

[3] Davis, *Ind. Eng. Chem.*, **20**, 1055 (1928).

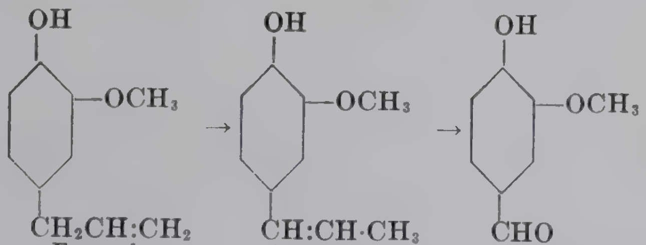
[4] Joubert and Norris, *J. Am. Chem. Soc.*, **51**, 873 (1929).

[5] Howes and Nash, *J. Soc. Chem. Ind.*, **49**, 113–119T (1930).

More drastic oxidation of the ethylenic bonds of oleic, linoleic, and similar unsaturated fatty acids causes the action to go beyond the formation of oxygenated groups and to result in rupture of the bond as well as in oxidation. Such agents as the dichromates, permanganates, and nitric acid may be used to obtain the effect. Thus, oleic,[1] dihydroxystearic, or sterolic acids[2] yield azelaic and pelargonic acids, products that may be further oxidized if the reaction is forced.

Isoeugenol to Vanillin.—The formation of vanillin from eugenol is an example of an oxidation of a side chain to an aldehydic group in which it is convenient to protect one substituent against oxidation. Eugenol obtained from oil of cloves is heated with an alkali such as sodium hydroxide to convert it to isoeugenol; the hydroxyl group protected by acetylation; and the substance oxidized and then saponified to vanillin.

The relatively slight difference in susceptibility to oxidation of the hydroxyl and propylene side chains makes it difficult to oxidize the propylene chain without affecting to some extent the hydroxyl substituent, unless it has been protected. Dichromates have been used to accomplish the oxidation step in this process of manufacture but are open to the objection that oxidation tends to go beyond the easily oxidized aldehyde stage with resultant formation of acids. The same is true of oxidation with permanganate. Less potent agents, such as nitrobenzene, have consequently been used for the direct oxidation of isoeugenol to vanillin.



Eugenol Isoeugenol Vanillin

Nitrobenzene has an advantage over more powerful oxidizing agents, such as the dichromates and permanganates, in the oxidation of isoeugenol to vanillin, as it does not induce such far-reaching oxidation of the desired aldehyde group to the undesired carboxylic group. Technically, the process may be conducted as follows: Eugenol from oil of cloves is dissolved in dilute sodium hydroxide solution, and the whole heated to 160°C. under pressure in an autoclave. This treatment converts the eugenol to isoeugenol and forms the sodium salt. For oxidation, 1 mole of nitrobenzene is added for each mole of eugenol originally transferred to the autoclave. Nitrobenzene is added slowly as the oxidation proceeds. After the reaction is complete, pressure on the autoclave is released, and the gaseous by-products are permitted to blow off. Vanillin may be recovered from the alkaline solution by precipitation with hydrochloric acid. The yield approximates 80 per cent of theory.

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[1] Green and Hilditch, *J. Chem. Soc.*, **1937**, 764.

[2] Grün and Wittka, *Chem. Umschau*, **32**, 257–259, (1925).

Isoborneol to Camphor.—Nitric acid has been widely used in the production of synthetic camphor from turpentine. The commonly accepted general practice for this manufacture (the one adapted by Gubelmann for use in this country) involves the following steps: (1) distillation of turpentine to obtain pinene; (2) saturation with HCl gas to obtain bornyl chloride; (3) hydrolyzing this to obtain camphene; (4) esterifying camphene to isobornyl acetate; (5) saponification to isoborneol; and (6) oxidation to camphor.

It is estimated that 12,000,000 lb. of camphor were produced in Europe during 1931 by this procedure, and the American production (roughly about 6,000,000 lb. annually) started in 1931.[1] The oxidation is performed as follows: 20 parts of isoborneol is dissolved in 100 parts of 1.32 sp. gr. nitric acid to which has been added 5 parts of 50 per cent sulfuric acid, and the mixture is heated with stirring at 80 to 90°C. (176 to 194°F.) for 10 hr. Other oxidizing agents, such as potassium permanganate, chromic acid, and nitric acid under other conditions, have not been found to be satisfactory.[2]

Isoborneol dissolved in benzene or chloroform is readily oxidized to camphor with chlorine. Thus, a solution of 15.4 parts of isoborneol dissolved in 16 parts of benzene is shaken violently with a solution of 7.1 parts of chlorine dissolved in 900 parts of water by weight. Violent agitation is necessary to secure intimate contact of the two immiscible solutions. Camphor is recovered from the benzene solution after reaction is complete, in almost quantitative yield, and contains only traces of chlorine. Use of alkaline aqueous solutions of chlorine results in the formation of sodium chloride as a by-product.

Aniline to Quinone.—Sodium or potassium dichromate may be used to oxidize aniline to quinone, but a low temperature and slow addition of the oxidizing agent must be employed in order to restrict the action. Although the high stability of the quinone structure toward further oxidation makes possible the use of so powerful an oxidizing agent as sodium dichromate in acid solution, care must still be exercised in order to prevent destructive reaction. An instance of the method is as follows: A mixture of 25 parts of aniline, 200 parts of water-white sulfuric acid, and 600 parts of water, contained in a wooden or corrosion-resistant vat, is cooled by ice or refrigeration. A solution of 25 parts of sodium dichromate in 100 parts of water is then slowly added with agitation, and stirring continued for 12 hr. A solution of 50 parts of sodium dichromate in 200 parts of water is then added, and stirring continued until the reaction is complete. During the whole operation, the temperature is maintained below about 5°C. through the addition of ice or by refrigeration. Quinone is recovered by skimming from the surface of the solution and purified by steam distillation.

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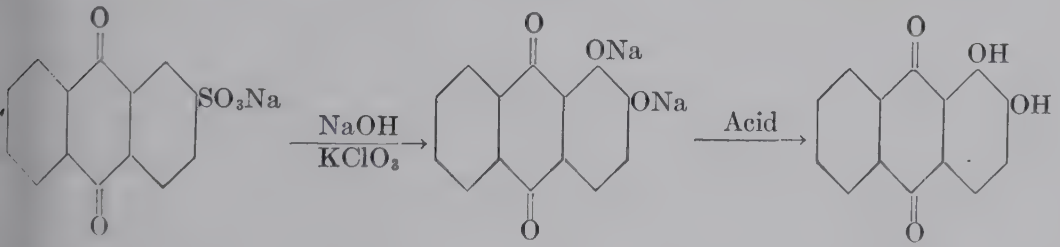
[1] GUBELMANN and ELLEY, *Ind. Eng. Chem.*, **26,** 589 (1934).

[2] BERI and SARIN, *Chemistry and Industry*, **1936,** 605.

Oxidation of aniline with MnO_2—H_2SO_4 mixtures is claimed to give 73 per cent yield of quinone.[1]

Quinone is readily reduced to hydroquinone, and much of the quinone that is manufactured is sold in the form of the hydrogenated product. Hydroquinone, in turn, is readily oxidized to quinone by such agents as chlorine, nitric acid, persulfuric acid, chromic acid, ferric chloride, and permanganates. The reduction of quinone to hydroquinone and the reoxidation of hydroquinone to quinone are very rapid processes and are strictly reversible. This reaction is one of the rare oxidation and reduction reactions of organic chemistry that are rapid and reversible like the oxidation and reduction of inorganic ions. Quinhydrone ($C_6H_4O_2 \cdot C_6H_4(OH)_2$) is formed as an intermediate in the process but is largely dissociated in solution. The dissociation is so rapid that quinhydrone acts like a mixture of quinone and hydroquinone, and an inert electrode in a solution of quinhydrone can be made to serve as a reference electrode, or half cell, if connected to another half cell. This property has led to the use of quinhydrone in the potentiometric determination of hydrogen-ion concentrations in unknown solutions.

Alizarin.—Potassium chlorate may be used as the oxidizing agent in the preparation of alizarin from anthraquinonesulfonic acid by the caustic-fusion process. For this purpose, 50 parts of the sodium salt of anthraquinone-β-sulfonic acid, *silver salt*, is stirred into 150 parts of sodium hydroxide and 150 parts of water contained in an autoclave, and 9 parts of potassium chlorate in 50 parts of water added. The substances are thoroughly mixed and heated in a closed autoclave for 30 to 36 hr. at a temperature of 170°C. The proportions of alkali may be modified so as to be but slightly in excess of theoretical; in which case, modifications in temperature and time are necessary for the practical operation of the process. The alizarin is precipitated from the solution at the boiling point by the



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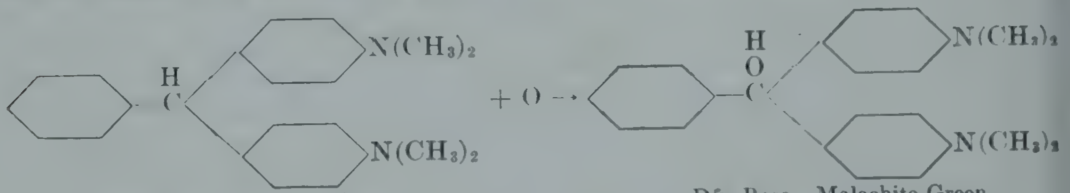
[1] Gibbs, U. S. 2,343,768 (1944).

addition of sulfuric or hydrochloric acid. The fine crystals obtained in this way are filtered from the hot solution and washed with hot water until free from salts. The dye is not dried but is made up as a 16 to 20 per cent paste and marketed as such. The yield is about 70 parts of alizarin from 100 parts of the *silver salt*, or about 90 per cent of theoretical.

Malachite Green.—Lead peroxide is principally used in the oxidation of leuco compounds of the triphenylmethane group to the corresponding alcohols, the salts of which are dyestuffs. Thus, malachite green may be prepared as follows:[1] 16.5 gm. of tetramethyldiaminotriphenylmethane is dissolved in 300 cc. of water and 20 gm. of concentrated hydrochloric acid. Sufficient ice is added to bring the volume to 400 cc. and the temperature to between 0 and 5°C. A lead peroxide paste made from 15.5 gm. of lead nitrate is slowly added while the solution is rapidly stirred. The reaction is complete in 2 hr., and the lead is precipitated by the addition of sodium sulfate solution and is filtered off. The dye base is precipitated, in the form of a resinous mass, by the addition of 15 gm. of caustic soda and is recovered by filtration. For use, the base is converted to a crystalline salt of oxalic or sulfuric acid.



Leuco Base Malachite Green Dye Base Malachite Green

Methyl Violet.—Cupric sulfate is employed in the formation of methyl violet from dimethylaniline. The process may be performed as follows: 600 to 800 parts by weight of finely divided sodium chloride is mixed with 50 parts of finely divided cupric sulfate, and a solution of 40 parts of phenol and 10 parts of water is added and stirred in; 100 parts of dimethylaniline is then added, and the mixture heated to 55 to 60°C. for 8 hr. or more. The hot product is poured or forced out of the reaction vessel and allowed to cool. The cooled product is broken up and added to 3,000 parts of boiling water to which 40 parts of calcium oxide has been added. The mixture is heated until free from lumps and settled, and the clear solution of salt and calcium phenoxide decanted off. The dye is recovered from the residue and purified by successive solution and salting out.

Oxidation of Toluene.—The use of manganese dioxide for the oxidation of toluene to benzaldehyde and benzoic acid was formerly extensive.[2]

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[1] Fierz-David, "Grundlegende Operationen der Farbenchemie," 2d ed., p. 153, Verlag Julius Springer, Berlin, 1922; "Dye Chemistry," p. 145, trans. by Mason, Churchill, London, 1921.

[2] Raschig, *Chem. Ztg.*, **24**, 346 (1900); Monnet, *Chem. Ztg.*, **22**, 929 (1898); **23**, **872** (1899); Fr. 276,258.

With manganese dioxide, the principal product is benzaldehyde; for high yields of benzoic acid, a stronger oxidizing agent such as chromic acid is required. For benzaldehyde production, the reaction is usually carried to the point where about 50 parts of benzaldehyde and 250 parts of toluene are recovered from a batch operation starting with 300 parts of toluene. In order to prevent extensive oxidation to benzoic acid, oxidation is not carried further than this. The method is as follows: 300 kg. of toluene and 700 kg. of 65 per cent sulfuric acid are mixed with intense stirring, and then 90 kg. of finely powdered manganese dioxide added while the temperature is held at 40°C. Benzaldehyde is recovered by steam distillation and constitutes a chloride-free product. Benzoic acid forms as a by-product.

This method has been modified so that manganese ammonium sulfate ($Mn_2(SO_4)_3 \cdot (NH_4)_2SO_4$) is first electrolytically oxidized in dilute sulfuric acid solution and then mixed directly with toluene at 50°C.[1] About 80 per cent of the toluene is oxidized to benzaldehyde. The manganese solution is recirculated through the oxidizing cell and reused. This process also yields a chloride-free product.

Adipic Acid.—Various methods have been proposed for the preparation of adipic acid by air or nitric acid (NO_2) oxidation of cyclohexane, cyclohexanol, cyclohexanone, cyclohexylamine, etc. For example, 12 gm. of cyclohexanone dissolved in 32 gm. of cyclohexane, slowly added to a mixture of 33 gm. of cyclohexane and 50 gm. of 60 per cent nitric acid and reacted at refluxing temperature for 1 hr., produced 13 gm. of adipic acid plus 4 gm. of lower dicarboxylic acids.[2] Reaction of 100 gm. cyclohexanol and 184 gm. of NO_2 for 2 hr. at 150°C. resulted in formation of 82.8 gm. of adipic acid (56 per cent yield on basis of cyclohexanol used).[3]

IV. LIQUID-PHASE OXIDATION WITH OXYGEN

The oxygen of the air is the cheapest available oxidizing agent but, at the same time, is perhaps the most difficult to control. Although atmospheric oxygen is constantly reacted with organic substances at ordinary temperature, the rates of the reactions are too slow, generally, to be of any significance from the standpoint of usefulness in chemical synthesis. To induce molecular oxygen to react at commercially useful rates, it is usually necessary to provide a catalyst, to elevate the temperature, or to use a catalyst in conjunction with elevated temperatures. In many cases, the temperature must be elevated to the point where vapor-phase processes only are practicable. These will be dealt with later.

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[1] Lang, *Chem. Zentr.*, **79,** I, 73 (1908); Ger. 189,178 (1907).

[2] Cavanaugh, U. S. 2,291,211 (1942); Cavanaugh and Nagle, U. S. 2,343,534 (1944); Meier, U. S. 2,300,955 (1942).

[3] Kenyon and Heyl, U. S. 2,298,387 (1942).

In liquid-phase processes, catalysts may be either dissolved or suspended in finely divided form to ensure contact with bubbles of gas containing oxygen which may be caused to pass through the liquid undergoing oxidation. To speed up production, means must be provided for initially raising the temperature and for later removing reaction heat. Where low temperatures and slow reaction rates are indicated, natural processes of heat flow to the atmosphere may suffice for temperature control.

Acetaldehyde to Acetic Acid.—The formation of acetic acid furnishes an excellent example of liquid-phase oxidation with molecular oxygen. Acetic acid may be obtained by the direct oxidation of ethanol, but the concentrated acid is generally obtained by oxidation methods from acetaldehyde that may have been formed by the hydration of acetylene or the oxidation of ethanol.[1] The oxidation usually occurs in acetic acid solution in the presence of a catalyst and at atmospheric or elevated pressures. Temperatures may range up to 100°C., depending upon conditions, but are usually lower.

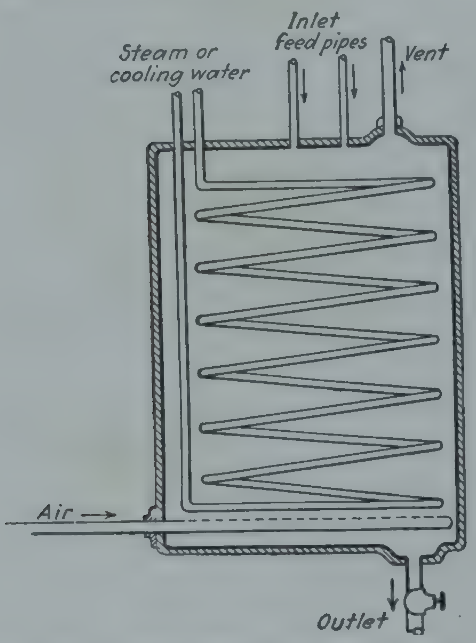

Fig. 1.—Apparatus for batch liquid-phase oxidation of acetaldehyde to acetic acid.

Figures 1 and 2 show the general type of apparatus used. The reaction vessel consists principally of an aluminum-lined steel vessel capable of holding 4,000 to 5,000 kg. (about 9,000 to 11,000 lb.) of acetaldehyde and fitted with aluminum coils for heating and cooling, inlet and outlet openings, and an air distributor.[2] In operation, about 4,500 kg. (about 10,000 lb.) of 99.0 to 99.8 per cent acetaldehyde previously cooled to 0 to 5°C. is first introduced, and then 18 to 22 kg. (about 39.6 to 48.4 lb.) of manganese acetate is added either in the form of a saturated acetic acid solution or as a powder ground to pass a 200-mesh sieve. Air is introduced through the distributor head, and, at the same time, steam is passed through the aluminum coils to raise the temperature gradually to the operating point. When reaction starts, oxygen absorption from the incoming air is almost complete, and the heat of reaction must be removed by cooling water, which is substituted for the initial steam. The temperature is so controlled that after 1 hr., it approximates 27°C.; after 2 hr., 28 to 30°C.; and after 4 hr., 60°C. The most satisfactory operating temperature is about 60°C. Reaction is complete in about 12 to 14 hr. The pressure is not allowed to exceed 5 kg. per sq. cc. (65.3 lb. per sq. in.), the nitrogen being vented through a series of condensers attached to the dome. Condensed aldehyde is returned to the kettle. Before being released, the nitrogen is passed through water scrubbers to remove the last of the aldehyde, which is later recovered. A concentrated acetic acid, exceeding 96 per cent in strength, results. Distillation is used for final concentration and purification of acid. The yield varies from 88 to 95 per cent of the theoretical. A retort of this size will produce about 60 tons of 99 per cent acid per month when operated normally or about 80 to 100 tons per month when forced.

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[1] See vapor-phase oxidation of ethanol, p. 456; see also Hale and Haldeman, Brit. 287,064 (1927); Fr. 650, 771 (1928); also, *Chem. Age*, **23,** 272–276 (1930).

[2] Cadenhead [*Chem. Met. Eng.*, **40,** 184–188 (1933)] states that 1,000-gal. kettles are used.

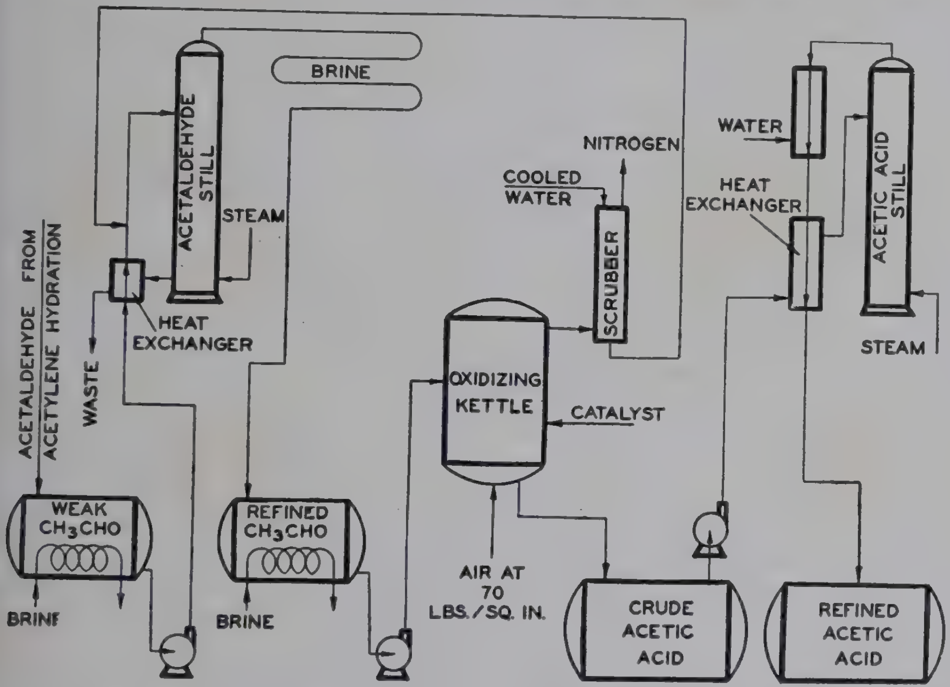
BRINE
ACETALDEHYDE STILL
STEAM
HEAT EXCHANGER
ACETALDEHYDE FROM ACETYLENE HYDRATION
WASTE
NITROGEN
COOLED WATER
SCRUBBER
OXIDIZING KETTLE
CATALYST
WATER
HEAT EXCHANGER
ACETIC ACID STILL
STEAM
WEAK CH_3CHO
BRINE
REFINED CH_3CHO
BRINE
AIR AT 70 LBS./SQ. IN.
CRUDE ACETIC ACID
REFINED ACETIC ACID

Fig. 2.—Flow sheet for oxidation of acetaldehyde to acetic acid.

To reduce the hazard introduced by possible formation of excessive concentrations of peracetic acid, efforts have been made to operate in such a way that the oxidized acetic acid-peracid-aldehyde solution is made to circulate through ceramic-packed towers against the gas stream containing unreacted aldehyde.[1] In this way, the acid may be built up in strength while low concentrations only of the peracid are maintained.

Acetaldehyde may be oxidized continuously to acetic acid by bubbling dry air upward through a body of reaction liquid 15 to 25 ft. deep at a temperature between 40 and 90°C. and a pressure between 100 and 200 lb. per sq. in. and comprising a 5 to 15 per cent solution of acetaldehyde in acetic acid containing a dissolved catalyst such as manganese acetate. The liquid is circulated continuously through coolers, fresh aldehyde being introduced to replace the acetic acid product withdrawn through a bleed line in the circulating system.[1] Introduction of air is such that substantially complete oxygen removal is accomplished.

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[1] Wiesler, U. S. 1,953,381 (1934).

In the presence of catalysts, such as the acetates of the eighth group of metals, particularly cobalt, oxidation of acetaldehyde by air to acetic anhydride is claimed to occur directly at temperatures of 30 to 35°C. and to result in 85 to 95 per cent conversions per pass.[2]

Ethanol to Acetic Acid.—The liquid-phase oxidation of ethanol by the quick-vinegar process has been widely practiced. In this case, the presence of *Mycoderma aceti* is used to convey oxygen to the alcohol and effect oxidation. In the early practice of the quick-vinegar process, wooden tanks about 3 to 4 ft. in diameter and 8 to 10 ft. high filled with beechwood shavings, other cellulosic material, or even coke which carry the microorganism *Mycoderma aceti* have been used. A dilute alcohol solution containing up to 12 to 15 per cent ethanol is allowed to trickle down over the packing material. Oxygen, as air, introduced at the bottom of the vat becomes heated from the heat of the reaction, rises, and passes out at the top. Functioning of the microorganism is best in a dilute acid solution and ceases at acid concentrations of about 12 per cent. A temperature of about 35°C. is most satisfactory. The product consists of a dilute acetic acid solution containing up to about 10 per cent acid. The small vats described are capable of producing up to about 8 gal. of this dilute acid per day. The size of vat has been dictated largely by difficulty of culture control. Improved processes at present permit the use of larger apparatus, and the trend is in this direction. One plant in this country is said to have a capacity for producing 10,000,000 lb. of acetic acid per year by this quick-vinegar process.[3] The best modern practice makes use of earthenware towers filled with beechwood shavings and fitted at the top with automatic spray devices for feeding in the dilute alcohol mixture or fermented mash solution.

Theoretically, 100 parts by weight of C_2H_5OH yields 130 parts of CH_3COOH by oxidation, equivalent to slightly over 1 kg. of acid per liter of alcohol. In practice, such 100 per cent yields are never obtained. Yields of 80 to 90 per cent of theory have been obtained in careful laboratory work, and 70 per cent yields are normally obtained in good industrial practice. The losses may be due to incomplete oxidation, to excessive oxidation through lack of proper control, and to volatilization of acid and alcohol in the stream of exit gases. The exit gases, after cooling, may be scrubbed with water, and the resulting solutions added to the feed.

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[1] Bardwell, U. S. 2,254,725 (1941).

[2] Hull and Marshall, U. S. 2,367,501 (1945).

[3] Partridge, *Ind. Eng. Chem.*, **23**, 488 (1931).

Pure ethanol exposed to air at normal temperatures does not undergo marked oxidation, but the introduction of platinum black causes oxidation to acetic acid. Other catalysts may also be used. Thus, the chemically catalysed oxidation of ethanol to acetic accompanied by acetaldehyde oxidation may be accomplished by use of acetic acid solutions with a cobalt acetate catalyst. In an example, 252 gm. of acetaldehyde was fed to the catalyst solution for activation, and then 85.4 gm. of 100 per cent ethanol together with air was introduced. Conversion of ethanol was 94.2 per cent to acetic acid, 3.5 per cent unchanged, and 2.3 per cent to ethyl acetate.[1] Temperatures below 145°C. were used. Various other metal acetates have been patented for the above process, including the salts of alkali and alkaline earth groups,[2] salts of the platinum metals group,[3] and salts of the chromium metals group.[4]

Other Alcohols to Acids.—The use of acetic acid solutions of various metal salts, such as those of metals having periodic system numbers 25 to 29, metals of the platinum group, metals of the chromium group, and alkali and alkaline earth metals, is claimed to permit oxidation of propyl and butyl alcohols to the corresponding acids by a procedure similar to that described for ethanol.[5] With a catalyst mixture containing molybdenum, vanadium, and thorium, 500 gm. of *n*-butanol gave yields varying from 50 to 400 gm. of butyric acid plus 0 to 20 gm. of propionic acid.

Oxidation of Aliphatic Hydrocarbons and Derivatives.—The use of dissolved catalysts, promoters, and initiators in a solvent of both the products and the hydrocarbon being oxidized facilitates the air (oxygen) oxidation of the lower aliphatic hydrocarbons. Such a technic permits the use of liquid-phase conditions, simplifies the problem of maintaining uniformity of temperature and removal of reaction heat, and permits regulation of the oxidation by control of pressure and rate of air or oxygen introduction. In such a process, Loder makes use of various liquids as solvents, preferably organic acids relatively inert to oxidation, catalysts such as salts of Ce, Co, Cu, Mn, V, U, Fe, plus promoters such as salts of Ba, Mg, K, plus "initiators" such as peroxides, peracids, aldehydes, ketones, olefins, or organic substances forming peroxides.[6]

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[1] Hull, U. S. 2,287,803 (1942).

[2] Hull, U. S. 2,353,157 (1944).

[3] Hull, U. S. 2,353,159 (1944).

[4] Hull, U. S. 2,353,160 (1944).

[5] Hull, U. S. 2,287,803 (1942); U. S. 2,353,157 (1944); U. S. 2,353,159; 2,353,160 (1944).

[6] Loder, U. S. 2,265,948 (1941).

As an example of the above process, with a cobalt acetate catalyst, diethyl ketone initiator, and acetic acid solvent, the air oxidation of isobutane at 100 to 155°C. and 50 atmos. pressure resulted in the reaction of 338.3 gm. out of 1131.8 gm. of isobutane charged to give a product containing acetone, 68.8 gm.; methyl acetate, 48.2 gm.; isobutyl acetate, 31.1 gm.; isobutanol, 47.1 gm.; unidentified, 18.1 gm.; water, 40.1 gm.; and a net gain of 13 gm. acetic acid.

Similarly, the oxidation of olefins with or without functional groups results in the formation of useful compounds.[1] Thus, oxidation of allyl acetate or chloride results in formation of glycerol, of mixed octylenes in formation of octylene glycols, of ethyl crotonate in methyl glycerol, etc. Unsaturated or hydroxylated long-chain fatty acids and their esters may also be oxidized by this process with resultant simultaneous oxidation and chain cleavage to yield aliphatic dibasic acids and aliphatic monohydroxy-monocarboxylic acids.[2]

The oxidation mass in processes such as the above applied to either aliphatic- or alkyl-substituted aromatics is extremely corrosive, and, in the experimental work, use was made of tantalum-lined reaction vessels. It has been found possible to use chromium-bearing steel for the reaction vessel if suitable proportions of lead or barium salts are present in the reaction mixture.[3]

The use of temperatures below the critical of the hydrocarbon being oxidized together with pressures adequate to maintain liquid-phase conditions gives advantages similar to the solvent process.[4]

Oxidation of Liquid Petroleum Hydrocarbons.—The oxidation of the higher members of the naturally occuring hydrocarbons of petroleum was one of the first reactions to be studied in the utilization of such substances as organic intermediates. The use of soluble salts of metals such as manganese, copper, iron, chromium, and vanadium permits operating temperatures from 100 to 160°C. in liquid-phase processes in which air or gaseous oxygen is contacted with the liquid hydrocarbon. Interest in such oxidations has centered quite largely in the formation of fatty acids, usually hydroxy or aldehydic in nature, suitable for the production of soaps, fats, esters, solvents, etc., or capable of hydrogenation of high-molecular-weight alcohols, which after sulfonation are, in turn, suited for use as detergents. Considerable of this work has centered on the oxidation of paraffin wax and comparable molecular-weight hydrocarbons.[5] It is reported that some 100,000 tons per year of fatty acids were produced by oxidation of various hydrocarbons in Germany during the Second World War.[1]

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[1] Loder, U. S. 2,316,604 (1943).

[2] Loder and Salzberg, U. S. 2,292,950 (1942).

[3] Henke and Benner, U. S. 2,276,774 (1942).

[4] Owen and Parker, U. S. 2,287,125 (1942).

[5] *Oil Gas J.*, **164**, No. 7, 130–139, No. 8, 145–151, No. 9, 69–77 (1945); *Soap and*

Many difficulties have been encountered, and progress has been slow. The acids tend to be aldehydic or hydroxylated in character; undesirable esters and other oxygenated compounds are formed; gums tend to be deposited; polymerization and condensation reactions that occur during the subsequent saponification operations give undesirable colors and odors to the product; separation of unoxidized hydrocarbons from the products is often difficult; etc. Volatile compounds, other than carbon oxides and steam, also form and may be recovered from the gases leaving the oxidation zone. Small quantities of the lower fatty acids, such as formic, acetic, and propionic, are produced and may be recovered with the water-soluble volatile products by scrubbing the exit gases with water or by extracting the oxidation mass with water.

In general, soluble catalysts have been used in the form of fatty acid salts, alcoholates, etc., of the metals capable of existing in combination in more than one valence form. Manganese compounds, such as the acetate or stearate, form good examples of the catalyst types. Cobalt and mercury catalysts tend to increase gum formation, and lead catalysts are of low activity. Catalyst mixtures consisting of at least one compound of an alkali metal and of aluminum have been found effective.[2] With 1 per cent manganese stearate in a paraffin wax, it is possible to oxidize at a temperature of 125°C. by injecting air, so that after 18 hr. a product with a saponification number of 232 and an acid number of 108 is obtained. As much as 15 to 20 per cent unsaponifiable matter remains in the product, even after prolonged injection of oxygen.[3] Without catalysts, oxidation does not start at a useful rate until a temperature of 150 to 160°C. is reached and does not become rapid until somewhat higher temperatures have been attained.

Even with a catalyst, long periods of time are necessary for the oxidation of a batch of oil or wax to approach completion when air is simply bubbled through the liquid. If very intimate contact is brought about between air and the hydrocarbon oil to be oxidized, through the formation of a foam of the liquid, the time of oxidation and the temperature for oxidation are both considerably reduced, losses through formation of low-molecular-weight oxidation products decreased, and the yield and quality of product increased. One method proposed for

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Sanitary Chemicals, **XXI**, No. 8, 38–39, 70, 78 (1945); NAMETKIN and ZVORYKINA, *Nat. Petroleum News*, **33**, No. 40, R702–708.

[1] *Chem. Eng. News*, **23**, 1520 (1945); T.O.M. Rept. No. 44.

[2] Dietrich and Luther, U. S. 2,000,222 (1935).

[3] ZERNER, *Chem. Ztg.*, **54**, 257–259, 279–281 (1930); ANON., *Chem. Age*, **23**, 254–255 (1930).

accomplishing this end is shown in Fig. 3. Admission of air through a porous diaphragm, properly placed, is used to induce a frothy condition in the material being oxidized, and a portion of the reacting material is recirculated through an external heat exchanger for temperature control. By continuously admitting unoxidized material and withdrawing oxidized product in regulated streams, the process may be made continuous. Either dissolved catalysts or solid catalysts fixed in place with fluid passing over them may be used.[1] Oxidation of crude paraffin wax (m.p., 50°C.) with air in the presence of dissolved manganese catalyst for 8 hr. at 110 to 115°C. in such an apparatus yields a yellow product having an acid number of 95 and a saponification number of 152. Light-colored fatty acids having a saponification number of 220 may be recovered. Since the rate of reaction increases with increase in oxygen concentration, the use of enriched air, oxygen, or air under pressures of from 150 to 500 lb. per sq. in. has been advocated. To reduce the troublesome polymerization and condensation reactions attending the oxidation, the liquid hydrocarbon may be diluted with oxidation-resisting substances such as acetic anhydride or other low-molecular-weight organic acids or anhydrides.

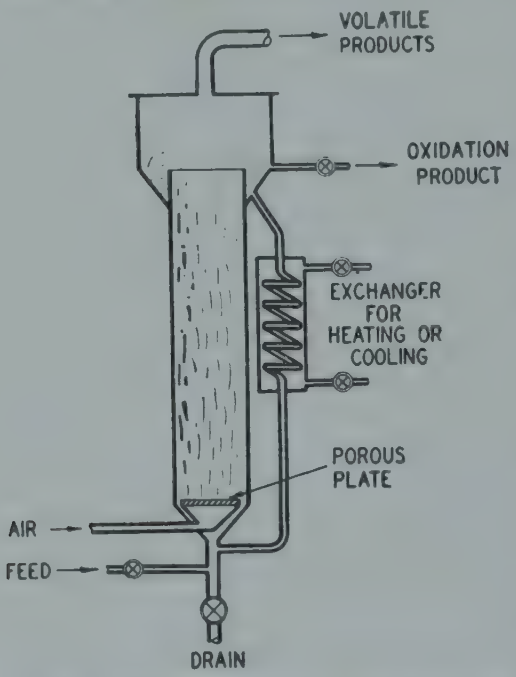

FIG. 3.—Arrangement of apparatus for liquid-phase oxidation of hydrocarbons to fatty acids.

The composition of the product is generally so complex as to defy chemical analysis for identification of the constituent compounds.[2] It is consequently difficult to postulate any definite series of reactions for the oxidation. Based on the experience of the I. G. Farbenindustrie A-G, however, tentative scheme has been proposed by Krauch for the oxidation mechanism by postulating that oxygen attacks the paraffin molecule toward the middle and not on the ends.[3] This proposal is supported by the facts that a portion of the acids formed contains about half the number of carbon atoms as the original paraffin molecule and that the small amounts of carbon oxides and low-molecular-weight oxidation products preclude oxidation from one end of the large molecules to form the acids in the product.

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[1] Luther and Goetze, U. S. 2,015,347 (1936); U. S. 2,095,338 (1937); Keunecke, U. S. 2,095,473 (1937).

[2] COLLIN, *J. Soc. Chem. Ind.*, **49**, 333T (1930).

[3] KRAUCH, *Proc. 2d Intern. Conf. Bituminous Coal*, **I**, 43 (1928).

The formation of an acid product having an average chain length of 12 to 14 carbon atoms, as calculated from the equivalent weight of the acid product from a paraffin wax averaging 24 carbon atoms per molecule, would seem to substantiate this postulated mechanism.[1] However, the fact that such an acid product consists of a variety of acids of varying chain length makes it seem more probable that the oxygen attack is distributed and that rupture may occur at various points in the affected molecules. This action of oxygen on the high-molecular-weight paraffinic hydrocarbons at moderate temperatures and in the liquid phase is contrary to that noted in the vapor-phase oxidation of the lower molecular-weight hydrocarbons at more elevated temperatures, where oxidation starts at the end of the longest carbon chain present in the molecule and continues from this point. The small amount of gaseous products obtained in the liquid-phase process precludes the possibility that the lower molecular-weight products are produced by the progressive destructive oxidation of the high-molecular-weight starting material, and the low temperatures seem to eliminate the possibility that thermal decomposition can account for the low-molecular-weight material obtained.

Naturally, separation and recovery of the desired fatty acids are difficult from such mixed products, and many recovery processes have been patented. Thus, extraction of the acid portion of such oxidation product with concentrated phosphoric acid permits separation of the hydroxylated acids from the fatty acids.[2] The organic acids are usually removed from the unoxidized hydrocarbon, alcohols, aldehydes, ketones, esters, etc., by saponification with an alkali and extraction as a water-soluble soap.[3] The use of morpholine soaps in separating the acids has been patented.[4]

The noncatalytic oxidation of hexadecane with air under a pressure of 13.6 atmos. at temperatures in the range of 190 to 300°C. has been shown to yield materials which, when hydrogenated, gave alcohols having molecular weights as high as 165.[5] Conversions of 17 per cent for the two-step process were obtained. A temperature approximating 250°C. was found most suitable for reaction. Air and hydrocarbon, in the ratio of 0.5 mole O_2 per mole of hexadecane, were passed to the bottom of a narrow, glass-lined reaction tube immersed in a heated salt bath and flowed up the tube as a mixture. Products were withdrawn through cooling tubes. Exposure time at reaction temperature varied from less than 4 to about 14 min.

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[1] Burwell, *Ind. Eng. Chem.*, **26**, 204–207 (1934).

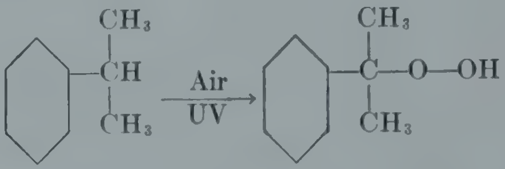
[2] Vesterdal, U. S. 2,038,617 (1936).

[3] Beller and Luther, U. S. 1,931,859 (1933).

[4] Zellner, U. S. 2,342,028 (1944).

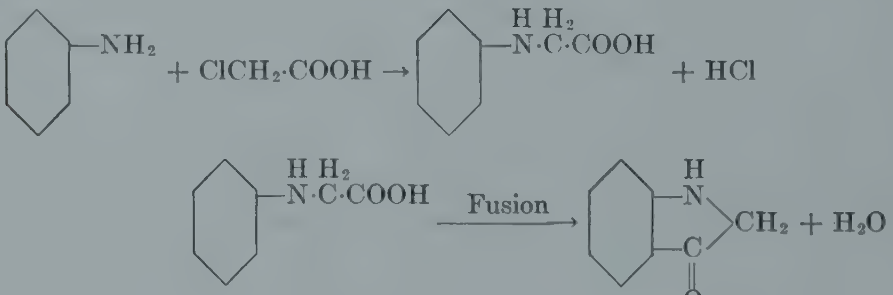
[5] Hass, McBee, and Churchill, *Ind. Eng. Chem.*, **37**, 445 (1945).

Under certain controlled conditions, it is possible to obtain substantial yields of peroxides from the air oxidation of hydrocarbons. Commercially available peroxides obtained from liquid-phase air oxidation of hydrocarbons are sold under the name "Uniperox" and find use as diesel fuel additives and polymerization catalysts.[1] Thus the autoxidation of isopropylbenzene (cumene) at elevated temperatures and with brief UV irradiation is comparatively rapid, occuring at the labile H atom of the isopropyl group. Thus:



Isopropylbenzene peroxide is a liquid comparatively stable to heat, decomposition beginning to set in at 165 to 175°C. The following peroxides also are described: isopropylbenzene-hydroperoxide, diphenylmethane-hydroperoxide, autoxidation of indene, and cleavage of tetralin-peroxide.[2]

Indigo Synthesis.—Another example of air oxidation is to be found in the indigo synthesis. Chloroacetic acid is condensed with aniline to form phenylglycine which, when fused with sodamide, loses a molecule of water and forms indoxyl. The red-brown melt obtained in the fusion of phenylglycine,



Phenylglycine

Indoxyl (Keto Form)

sodamide, and sodium hydroxide is dissolved in a large volume of water. Air is then blown through this alkaline solution for several hours, and the indoxyl becomes oxidized to indigo which separates out in small crystals. The indigo is recovered by filtration, and the crystals washed

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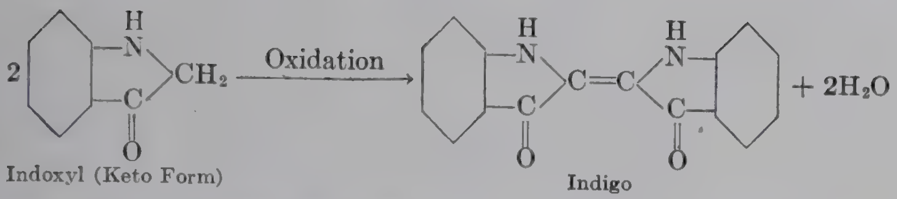
[1] FARKAS, SMITH and STRIBLEY, Presented before Petroleum Division, 109th A.C.S. Meeting, Atlantic City, N. J. April 8–12, 1946.

[2] HOCK and LANG, *Ber.*, **76B**, 1130–1131 (1943); *Ber.*, **77B**, 257–264 (1944).



and made up to a paste with water. A yield of close to 90 per cent of theory is obtained.

This capacity to undergo ready oxidation in alkaline solution is made use of in the dyeing of fabrics with indoxyl. In practice, the indigo is reduced to the leuco base, which is water soluble, and the fabric to be dyed is soaked in an alkaline solution of this dye base. Exposure of the fabric to the air fixes the dye by the oxidation of the leuco base to the insoluble indigo blue. Such a process is known as vat dyeing, and indigo is one of the most important of the dyes applied in this manner.

Cyclohexane.—The importance of adipic acid as an intermediate in the manufacture of nylon and the polyamid plastics has created considerable interest in its formation by the oxidation of cyclohexane or products derived therefrom.[1] For the direct oxidation of cyclohexane to adipic acid (or of cyclopentane or cyclobutane to corresponding dicarboxylic acids), it has been found that oxidation catalysts consisting of salts of metals having atomic weights between 50 and 200, *e.g.*, cerium, cobalt, copper, manganese, and uranium, used in the presence of an organic acid solvent for the hydrocarbon and with the help of a peroxide reaction-initiator permit the recovery of up to 50 per cent yields of the dicarboxylic acid at temperatures of about 100°C.[2] Air is introduced by bubbling through the liquid mixture for periods up to 5 or 6 hr.

The use of milder conditions for the oxidation in a process similar to the above, such as lower temperatures, lower oxygen concentrations, or less active catalysts, results in the formation of cyclohexanone and cyclohexanol.[3] Based on oxygen consumed, the conversions to cyclohexanone approximate 90 per cent or more.

Cyclohexanone may be air-oxidized to adipic acid with yields of 60 to 70 per cent of theory by use of organic acid solutions of active metal salts modified by salts of alkali or alkaline earth metals as catalysts.[4] Air bubbled through an acetic acid solution of cyclohexanone that contained 0.066 per cent manganese acetate and 0.155 per cent barium acetate, based on weight of acetic acid, gave yields of about 70 per cent adipic acid at conversions of about 60 per cent.[5]

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[1] See page 445 for adipic acid by nitric acid oxidation.

[2] Loder, U. S. 2,223,493 (1940).

[3] Scott and Walker, U. S. 2,223,500 (1940); Drossbach, U. S. 2,285,914 (1942).

[4] Amend, U. S. 2,316,543 (1943).

[5] Machinskaya and Veselovskaya, *J. Appl. Chem.* (*U.S.S.R.*), **17**, 377–379 (1944).

V. VAPOR-PHASE OXIDATION OF ALIPHATIC COMPOUNDS[1]

Almost without exception, the vapor-phase processes employed in the partial oxidation of organic compounds use molecular oxygen as the oxidizing agent and require catalysts and elevated temperatures for operation at industrially useful rates. Only certain substances are fitted for vapor-phase processing. These must have sufficiently high vapor pressures at the temperatures required for oxidation to make it possible to mix them with air (oxygen) and pass them in the gaseous state over the catalyst material. They must be of sufficient thermal stability to resist undesired decomposition and give rise to products of comparable thermal stability. Furthermore, the products must be reasonably stable to continued oxidation and must be readily recoverable from the gaseous products.

It will be found that these various restrictions limit the materials capable of economic processing by vapor-phase oxidation to the simpler aliphatic compounds and the aromatic series of compounds. Because the methods applied to these two classes of compound are characterized by consideration for group properties, they will be treated separately.

Oxidation of Methanol.[2]—Consideration of the reactions involved in the synthesis and decomposition of methanol shows that only low conversions to formaldehyde may be obtained by the direct catalytic decomposition of the alcohol.

$$CH_3OH \rightarrow H_2CO + H_2 \rightarrow CO + 2H_2$$

Catalysts and temperatures conducive to the dehydrogenation of methanol are also conducive to the decomposition of the formaldehyde to hydrogen and carbon monoxide. Furthermore, the reaction is endothermic, and heat must be supplied.

However, if oxygen, in the form of air, is furnished to the reaction, and the process conducted in the vapor phase in the presence of suitable catalysts, industrially practicable yields of formaldehyde are obtained, and the process is made exothermic. Practically all the formaldehyde used today is produced in this way. Although the process appears simple, it requires regulation of temperature, air-to-alcohol ratio, and time of contact to ensure continuous high yields at high efficiency. A simple, practical method consists in mixing air with methanol, passing the resulting air-methanol mixture over a hot copper-gauze catalyst (see

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[1] Sections V, VI, and VII are based on parts of the *Am. Chem. Soc. Monograph* 61 (1932), "Catalytic Oxidation of Organic Compounds in the Vapor Phase," by Marek and Hahn. Use has been made of text and illustrations through the kind permission of the publishers, Reinhold Publishing Corporation, New York.

[2] WALKER, "Formaldehyde," *Am. Chem. Soc. Monograph* 98 (1944), Reinhold Publishing Corporation, New York.

Fig. 4), condensing the gaseous reaction mixture, and recovering the product.

For oxidation to formaldehyde, 1 lb. of pure methanol theoretically requires 26.7 cu. ft. of dry air measured under standard conditions (2.18 lb.). When air is bubbled through the liquid methanol, this proportion can be only approximately maintained, and more positive methods of control are needed. Exact control of the ratio is made possible by the use of separate, controlled streams of air and liquid methanol introduced to a vaporizing chamber, which is supplied with heat to vaporize the liquid. Cleaned, dry air is supplied through a storage tank by a compressor, and methanol enters the mixing chamber as a liquid. Only small amounts of mixed air and vapor are present at any time; the mixture passes immediately to the catalyst chamber and thence to the recovery system.

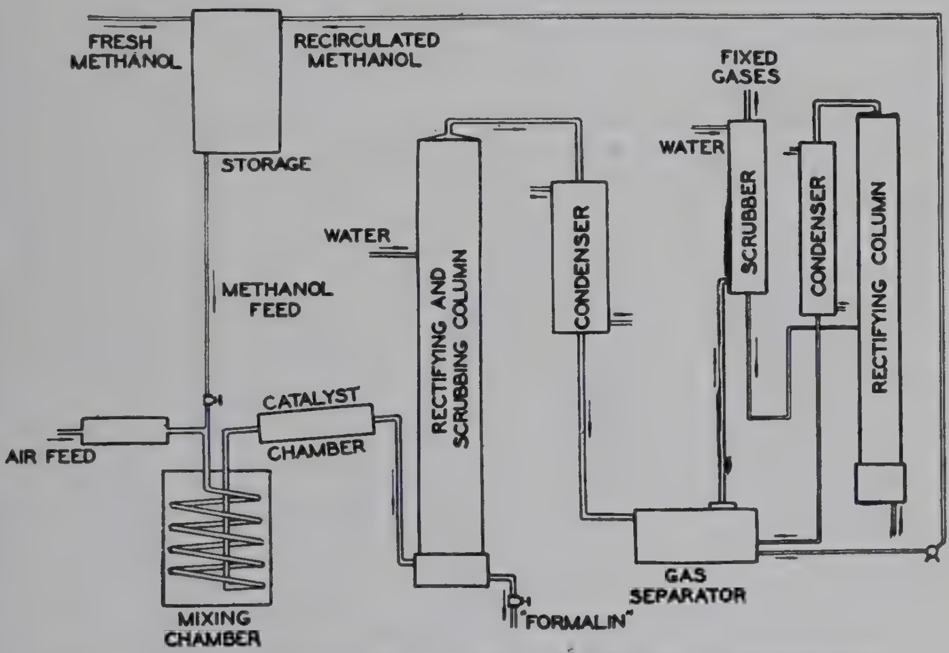
FRESH METHANOL
RECIRCULATED METHANOL
STORAGE
FIXED GASES
WATER
SCRUBBER
CONDENSER
RECTIFYING COLUMN
WATER
RECTIFYING AND SCRUBBING COLUMN
CONDENSER
METHANOL FEED
CATALYST CHAMBER
AIR FEED
MIXING CHAMBER
GAS SEPARATOR
"FORMALIN"

Fig. 4.—Schematic layout for oxidation of methanol to formaldehyde.

Large amounts of formaldehyde have been made with a catalyst generally consisting of copper arranged in the form of gauze rolls supported in concentrically arranged bundles of copper tubes, which, in turn, are held by headers on each end. Such a catalyst chamber may consist of six or eight copper tubes 24 in. long and 2 in. in diameter containing rolled-up copper gauze for about 4 or 5 in. of their length, fitted into suitable headers at each end and enclosed in a cover. Means are provided for heating the catalyst mass at the start of operation. Reaction occurs at a temperature of 400 to 450°C., and operation is conducted at a temperature of about 550 to 600°C. in the catalyst mass. The rate of feed and the air-methanol ratio are maintained so as to make operation autothermal. The gaseous mixture passes from catalyst chamber to a rectifying and recovery system, where rapid countercurrent cooling is obtained by contact with the relatively cool aqueous formaldehyde solution that passes down the column. Formaldehyde solution is withdrawn at the bottom of the column, and fixed gases containing the vapor of unreacted methanol are passed out of the top to a condenser where the methanol is partly recovered. The fixed gases from this condenser are scrubbed with water or dilute methanol solution for complete methanol recovery. Condensed methanol and methanol recovered from the aqueous solution by rectification are fed back to the mixing chamber for recirculation over the catalyst. Methanol containing very little formaldehyde may be obtained by the rectification of solutions containing as much as 38 per cent of formaldehyde so as to leave very little methanol in the residual aqueous solution.

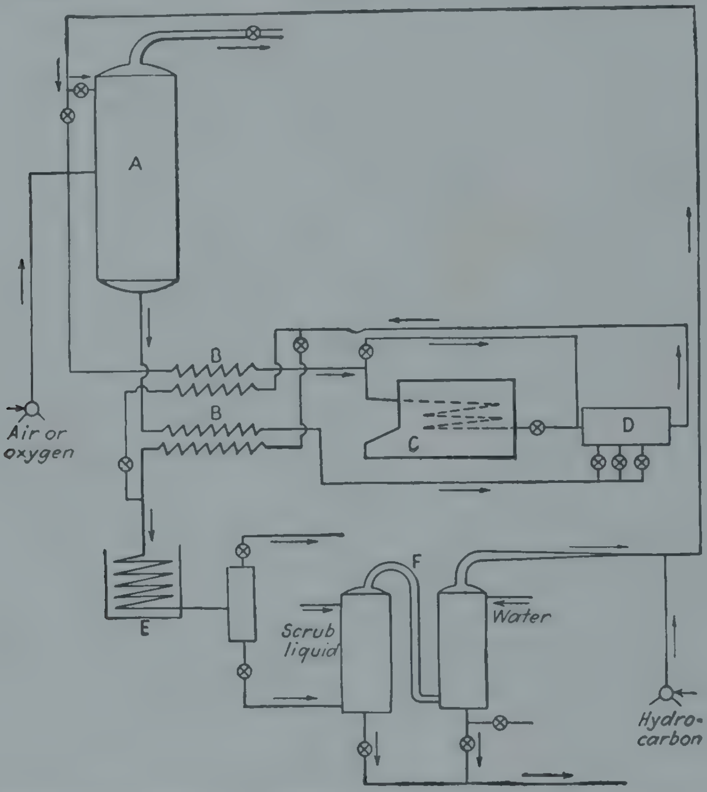

FIG. 5.—Schematic layout for pressure oxidation of aliphatic hydrocarbons.

A. Oxygen saturator.
B. Preheater (heat exchangers).
C. Furnace.
D. High-pressure reactor.
E. Cooler and gas separator.
F. Scrubbing system.

The development of more active and directive catalysts for methanol oxidation has resulted in important process improvements. The use of reaction temperatures of 300°C. (572°F.) or less, by means of catalysts such as molybdenum promoted with iron, vanadium, or other elements or vanadium promoted with an element of the fifth or sixth group of the periodic system, makes it possible to use multiple-tube reaction chambers with heat removal by circulated liquids (Fig. 9) and to employ air ratios such that more complete oxidation of methanol per pass is obtained without loss in yield.[1] Thus, it is possible to increase materially the capacity of a reaction unit; to reduce the by-product CO, CO_2, and acid produced; to increase the oxidation efficiency to a point where methanol need not be recovered and recirculated; and to increase the over-all process efficiency. By way of example, such an operation performed with a catalyst formed of a mixture of molybdenum trioxide and 8 to 20 per cent by weight of ferric oxide, screened to 8-mesh particles and packed 9 in. deep in a tubular catalytic chamber immersed in a heat-removing liquid bath at 250°C. (482°F.); with a reaction mixture of 8 to 10 per cent by weight methanol vapor and 90 to 92 per cent air (4.2 to 5.4 times theoretical air); and with a time of contact of 0.01 to 0.03 sec.) results in a 95 per cent conversion of methanol to formaldehyde and 5 per cent conversion to by-products comprised almost wholly of CO and CO_2.[2]

The water formed by reaction is not sufficient to bring the formaldehyde solution to the 37.0 to 37.5 per cent by weight concentration at which it is generally sold, and some water must be added. Commercial formaldehyde contains some 37 per cent H_2CO, about 9 per cent methanol, and 54 per cent water. This solution will not deposit polymer on standing, whereas one containing no methanol will deposit solid on slight cooling. Large commercial formaldehyde producers have now developed stabilizers that will permit production of full strength, stable formaldehyde without the use of methanol.

Formaldehyde also appears on the market as the hydrated, solid polymer *paraformaldehyde*, containing about 95 per cent formaldehyde, which is prepared by the evaporation of formaldehyde solution.

According to theory, 100 gm. of pure methanol should yield 93.75 gm. of pure formaldehyde, but, in practice, only about 82 to 85 per cent of theoretical yield is obtained. Conversions as high as 96 per cent are possible with laboratory methods and have been approached for short periods in commercial apparatus. At the ordinary conversion efficiency, 100 lb. of methanol yields between 190 and 200 lb. of commercial formaldehyde solution.

Oxidation of Ethanol.—Ethanol may be dehydrogenated or oxidized to acetaldehyde in the vapor phase with good yields. Various investigators have reported maximum conversions in the range of 70 to over 80 per cent. Commercially, this method of acetaldehyde production competes with the hydration-of-acetylene process and the direct oxidation of hydrocarbons. Copper- and silver-gauze catalysts are effective for oxidation,[1] and chromium-activated copper catalysts[2] for the dehydrogenation.

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[1] Meharg and Adkins, U. S. 1,913,404; 1,913,405 (1933); Punnett, U. S. 2,065,394 (1936); Craver, U. S. 1,914,557 (1933); 1,914,558 (1933); Punnett, U. S. 1,978,506 (1934); Bailey and Craver, U. S. 1,383,059 (1921); Downs, U. S. 1,604,739 (1926); *Chem. Age*, **42,** 48 (1940).

[2] Meharg and Adkins, *loc. cit.*

Difficulty has been encountered, however, in effecting the direct oxidation of ethanol to acetic acid in a continuous, catalytic, vapor-phase process. Losses to formaldehyde, carbon oxides, etc., are difficult to prevent. By the simultaneous oxidation of mixtures of acetaldehyde and ethanol in the vapor phase, it is claimed that good conversions are obtained of acetaldehyde to acetic acid and of ethanol to acetaldehyde, which is then recycled in the process. The greater the proportion of acetaldehyde to alcohol the lower may be the temperature for reaction.[3] Reaction of a mixture of 1 part by weight of ethanol, 1.077 of acetaldehyde, 1.055 of air, and 0.196 of steam by passage through a 60-ft. by 0.75-in. tube at 525°F. is said to yield a product containing 0.182 part by weight of acetic acid, 1.078 parts of acetaldehyde, and 0.855 part of ethanol. By recycling and introducing fresh ethanol, there is obtained 1.086 parts by weight of acetic acid, 0.091 part of acetaldehyde, and 0.095 part of ethanol for each part of ethanol fed to the system.

Oxidation of Other Alcohols.—In recent years, methyl vinyl ketone has received considerable attention as a possible component of various polymer products. Almost all the information regarding uses, preparation, methods of polymerization, stabilization, etc., of methyl vinyl ketone is contained in the patent literature.[4]

Catalytic dehydrogenation of methyl vinyl carbinol at temperatures above 250°C. in presence of a brass spelter catalyst is claimed to give a 33 per cent yield of methyl vinyl ketone, $CH_3{\cdot}CO{\cdot}CH{=}CH_2$.[5] Catalytic, vapor-phase oxidation of the unsaturated alcohols to form unsaturated carbonyl compounds has been found to give considerably higher yields.[6] Temperatures in the range of 360° to 550°C. and use of a metallic silver catalyst are described.

The use of vinyl acetylene, the commercial manufacture of which as an intermediate in the production of chloroprene is well established, can also be used as an intermediate for methyl vinyl ketone.[1] Reaction of vinyl acetylene with water in the presence of mercury salts and sulfuric acid catalyst has been reported to give 90 per cent yields of methyl vinyl ketone.[2]

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[1] Fuchs, U. S. 1,956,440 (1934).

[2] Young, U. S. 1,977,750 (1934).

[3] Bludworth, U. S. 2,263,607 (1941).

[4] See Breuer, "Review of German Patent Literature Relating to Synthetic Rubber," *Rubber Age*, **54**, 229–234 (1943); 336–340 (1945). Conaway, U. S. 2,088,577 (1937); Meisenburg, Bock, and Bächle, U. S. 1,937,063 (1933); Yale and Hearne, U. S. 2,398,685 (1946).

[5] Groll, U. S. 2,011,317 (1935).

[6] Groll and deJong, U. S. 2,042,220 (1936).

The oxidation of (alkoxyalkoxy) alcohols to prepare, for example, (methoxymethoxy) aldehydes has been claimed to occur readily in the presence of silver or copper gauze or the usual oxidation catalysts with either air or oxygen.[3]

Oxidation of Low-molecular-weight Paraffin Hydrocarbons.—Recent efforts toward the catalytic oxidation of low-molecular-weight hydrocarbons have been directed toward the control of oxygen concentration, temperature, and reaction rate by the use of selective catalysts and elevated pressures, with the purpose of stopping the oxidation at an intermediate stage where the products constitute useful substances. Examples of only a few representative cases will be given.

In the catalytic oxidation of aliphatic hydrocarbons at atmospheric pressure, the oxidation reactions are probably stepwise, each successive step occuring with greater ease. The type of reaction for the successive steps is the same, and, when a carbon compound containing oxygen is oxidized further, it is the hydrogen atoms joined to the carbon atoms already in combination with oxygen that are attacked.[4] Thus, the point of first attack continues to be the point for successive attacks. This has been clearly shown for the case of the oxidation of the isomeric octanes, where the methyl group at the end of the longest free straight chain is first attacked and the oxidation continues along the chain to a point where a resistance to further oxidation is encountered. At such a point—represented by formation of a ketone structure at the point where the chain branch ends in the case of the iso-octanes—oxidation may be partly arrested, and the product recovered before decomposition or oxidation can destroy it. However, a considerable portion of the hydrocarbon will have been destroyed when this point is reached; a large amount of heat will consequently have been liberated; and only a low yield of any single ketone will have been obtained from such a mixture of isomeric hydrocarbons.[5]

To obtain useful and desirable intermediate products of oxidation from the aliphatic hydrocarbons, it is necessary that only relatively small proportions of oxygen be made to react with the hydrocarbon molecule. However, this limited reaction is difficult of practical attainment; and with the normally gaseous straight-chain aliphatic hydrocarbons, almost regardless of molecular weight, appreciable yields of only formaldehyde have been reported to result from the oxidation in the presence of solid catalysts at atmospheric pressure. Alcohols have been obtained under certain special conditions to be discussed later, and ketones have been reported to result from the oxidation of branched-chain hydrocarbons. The higher molecular-weight aliphatic hydrocarbons, oxidizing more readily under less stringent conditions, may be converted to relatively long-chain acids, etc.

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[1] Nieuwland, Calcott, Downing, and Carter, *J. Am. Chem. Soc.*, **53**, 4197 (1931).

[2] Churbakov and Ryazantsev, *J. Appl. Chem.* (*U.S.S.R.*), **13**, 1464 (1940).

[3] Loder and Gresham, U. S. 2,307,934 (1943).

[4] Ewell has shown that the chlorination of paraffins follows a similar pattern.

[5] Pope, Dykstra, and Edgar, *J. Am. Chem. Soc.*, **51**, 1875–1879, 2203–2213 (1929).

The principal difficulty in dealing with methane, the most abundant of these gaseous hydrocarbons, is the unreactive nature of the substance. At the temperature required for active reaction between methane and oxygen, the desired products (methanol and formaldehyde) are thermodynamically unstable at a pressure of 1 atmos. The ignition temperature of methane in air is 695 to 742°C. and represents the temperature at which the rate of reaction between methane and oxygen is sufficiently rapid to make the reaction self-sustaining and capable of propagating through the combustible mixture. Somewhat lower temperatures may be used at the longer times of contact employed in partial oxidation, and application of catalysis is of benefit in lowering the reaction temperature further. However, even at the temperatures made possible through the use of catalysts, the products are largely unstable to dissociation and are made more subject to destruction through either increased reaction rate or continued oxidation. The net result of the use of solid catalysts has been, therefore, the increased rate at which methane may be made to react with very little benefit toward increased conversions of hydrocarbon to product at per-pass yields that would warrant industrial application.

Numerous materials have been reported and patented as catalysts for the oxidation of the gaseous paraffin hydrocarbons. The majority of these, consisting mainly of metals or metal oxides, are far too active and too nonspecific in action to permit the recovery of more than small amounts of intermediate oxidation product. With such relatively mild catalysts as copper oxide and glass surfaces, some high yields of formaldehyde have been obtained from methane and ethane under experimental conditions. Under conditions where less than 10 per cent of the entering hydrocarbon is oxidized, conversions of over 50 per cent of reacting hydrocarbon to formaldehyde have been reported. The necessity of recovering formaldehyde from such dilute gaseous mixtures as may be thus obtained and of recycling the unreacted hydrocarbon militates against the industrialization of the process. Furthermore, the use of air as a source of oxygen introduces inert nitrogen, which further serves to dilute the product. Even the use of pure oxygen permits an estimated recovery of methane as formaldehyde of only about 30 per cent—too low for commercial adaptation unless the hydrocarbon is available at practically no cost.[1]

In contrast to the relatively poor results obtained from the oxidation of methane, at low or atmospheric pressures, oxidation of natural gas with very low oxygen concentrations under slight pressure and in the presence of a catalyst, such as copper- copper oxide, has been shown capable of producing a useful mixture of oxygenated products, *i.e.*, formaldehyde, acetaldehyde, and methanol. Such a process, representing a by-product of the major industry of transporting natural gas, should be capable of yielding formaldehyde in competition with the usual method of forming it from methanol by oxidation.[2] The results are indicative of what may be accomplished by a modified direct-oxidation process.

The aliphatic hydrocarbons become progressively more easily oxidized as the number of carbon atoms in the free straight chain is increased. This is shown by a comparison of the ignition temperatures of several normal paraffin hydrocarbons. Thus:

Hydrocarbon	Ignition Temp.,[1] °C.
Methane	695–742
Ethane	534–594
Propane	514–588
n-Butane	489–569
n-Pentane	476–548

[1] International Critical Tables, III, 173.

As might be expected, higher yields of intermediate oxidation products, particularly formaldehyde, are obtainable from the oxidation of the higher members of the group.

An example of the controlled, noncatalytic oxidation of low-molecular-weight paraffin hydrocarbons to form commercially practicable yields of oxidation products is given by the process devised by Bludworth. In the oxidation of butane or other low-molecular-weight paraffin hydrocarbon, Bludworth uses a large excess of a diluent such as steam, a short reaction time, a limited proportion of air to hydrocarbon, and a water quench.[3] Examples taken from the patents show that under the given conditions, yields of products listed in the following table may be obtained:

A. Ratio by weight of 1 part of butane, 5 parts of air, and 34 parts of steam; preferred pressure range of 20 to 30 atmos.; temperature of 750°F.; time of reaction of 1.15 sec.; and quench to 300°F.

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[1] Ledbury and Blair, *Dept. Sci. Ind. Research* (*Brit.*) *Rept.* 1, 1–54 (1927).

[2] Brooks, *J. Inst. Petroleum Tech.*, **24**, 744 (1928); Burrell, *Nat. Petroleum News*, **22**, (22), 80 (1930).

[3] Bludworth, U. S. 2,128,908; 2,128,909 (1938); 2,369,710 (1944).

B. Ratio by weight of 1 part of butane, 5 parts of air, and 18.5 parts of steam (plus recycled unreacted hydrocarbon gases); preferred pressure range of 3.5 to 20 atmos.; temperature of 550°F.; time of reaction of 0.3 sec.

Products	Yields based on 100 parts butane	
	A, parts	*B*, parts
Acetaldehyde	19.6	23.0
Acetone	7.0	10.0
Methanol	19.0	3.0
Propanol	1.0	3.0
Butanol	0.5	3.0
Organic acids	11.4	7.0
Formaldehyde	15.2	15.0
Total	73.7	64.0

Any type of low-molecular-weight hydrocarbon is suitable for the process, such as butane, pentane, casing-head gasoline, and the C_3 to C_6 fraction of refinery gas.

All the products of oxidation are commercially useful; and when they are produced on a large scale, the possibilities of economic production are apparent. It has been proposed to utilize mixtures such as the foregoing for manufacture of additional acetic acid from the acetaldehyde and pentaerythritol from the formaldehyde and a portion of the acetaldehyde remaining in the aqueous solution after separation of the major portion of the acetaldehyde.[1]

The use of HBr as a gas-phase catalyst in the direct oxidation of various hydrocarbons has been shown to result in high yields of oxidation products.[2] Thus, reaction of a mixture of 2 parts by volume of propane, 2 parts of oxygen, and 1 part of HBr at 188°C. for 3 min. is claimed to result in a yield of 76 mole per cent acetone plus 11.2 mole per cent propionic acid based on propane consumed. A similar mixture, in which *n*-butane replaced the propane, reacted at 185°C. for 3 min. is claimed to yield 52 moles per cent methyl ethyl ketone and diacetyl. HBr is recovered from the reaction gases as the alkyl bromide and may be recycled. Oxidation of cyclopentane, cyclohexane, ethyl benzene, etc., is claimed to yield ketones by the process. Similar use of HBr as a catalyst at about 225°C. has been claimed to result in formation of acrylic acid and allyl bromide from propylene, crotonic acid from butene-2, cyclohexanone from cyclohexene, etc.[1] Hydrogen halide catalysts also promote the dehydrogenation of olefins to form diolefins in the absence of solid catalytic bodies.[2]

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[1] Bludworth, U. S. 2,333,696 (1943).

[2] Rust, U. S. 2,380,675 (1945).

Other vapor-phase oxidation catalysts include such "proknocks" as alkyl nitrates, nitrites, or nitro compounds,[3] nitric oxides.[4]

By conducting the oxidation of the low-molecular-weight paraffin hydrocarbons under high pressures, it has been possible to obtain alcohols, increased yields of aldehydes, and acids as oxidation products. Conditions claimed for the pressure processes include (1) pressures of 50 to 250 atmos.; (2) temperatures from 200 to 600°C.; (3) low oxygen-to-hydrocarbon ratios ranging from 5 to 15 mole per cent; with (4) short time of contact; and (5) the presence of a variety of catalysts. The more extreme conditions have been found necessary for the lower members of the paraffin series. Although the low proportions of oxygen may account for part of the effects that have been observed from pressure oxidation, the major results must be attributed to the effect of the elevated pressure.

One of the chief effects of the elevated pressures is the lowering of the reaction temperature and the consequent lessening of the tendency for thermal decomposition of the products. Thus, whereas the noncatalytic oxidation of methane requires a temperature of 600 to 700°C. at atmospheric pressure and results in the formation of formaldehyde as the least oxidized intermediate product obtainable in appreciable quantities, a temperature of only 360°C. is required for oxidation at 100 atmos. pressure with a 9:1 methane-oxygen ratio and the formation of methanol results. Comparable lowering of temperature has been obtained with the higher hydrocarbons. Pressure may also be effective in stabilizing the products.

Newitt and Haffner, working in Bone's laboratory, have been able to obtain considerable quantities of methanol by the slow combustion of methane at high pressures.[5] An 8.1:1 methane-oxygen (11 mole per cent oxygen) mixture was allowed to react in a steel chamber at different temperatures and pressures. Reaction appeared to be predominantly heterogeneous, since an increase in the surface-to-volume ratio of the chamber caused a several-fold increase in reaction rate. A pronounced induction period was observed, but no peroxides were found in the product. The effects of increasing the pressure from 48.2 to 150 atmos. were to increase (1) the rate of reaction or lower the temperature required for a given rate; (2) the amount of methanol and formaldehyde in the product; and (3) the ratio of methanol to formaldehyde in the product. In all cases, carbon monoxide and carbon dioxide represented upward of 70 per cent of the methane that reacted.

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[1] Rust and Vaughan, U. S. 2,369,182 (1945).

[2] Amos and Soderquist, U. S. 2,370,513 (1945).

[3] Thomas, U. S. 2,365,851 (1944).

[4] Nashan, U. S. 2,244,210 (1941).

[5] Newitt and Haffner, *Proc. Roy. Soc. (London)*, **A134**, 591–604 (1932).

Pichler and Reder have qualitatively confirmed the results of Newitt and Haffner on the pressure oxidation of methane but did not report as high yields on the basis of methane reacted.[1] However, these workers extended their experiments to include a series of flow runs at 100 atmos. pressure, at 500°C., and with various oxygen concentrations. These runs showed that a higher temperature was needed for reaction than in the case of the static (bomb) runs but that better yields were obtainable at comparable pressures. Conversion increased as the oxygen concentration was lowered, until at 0.6 per cent oxygen, about 60 per cent of the entering oxygen appeared in the product as methanol.

Table I.—Pressure Oxidation of Methane

Pressure, atmos.	Initial temp., °C.	Time, min.	Yield based on % of methane reacting to form	
			Methanol	Formaldehyde
10	400	10	1.1	None
25	385	7	4.8	0.66
40	372	15	6.1	1.20
48	373	4	13.7	0.8
106.4	341	12	22.3	0.75
149	341	16	19.0	0.60

Representative experimental results from pressure oxidation of ethane are shown in Table II.[2]

In general, the oxidized product from the pressure oxidation of hydrocarbons above methane in molecular weight may be expected to consist of a mixture of oxygenated organic compounds comprising alcohols, aldehydes, ketones, acids, esters, etc., together with water and carbon oxides. The recovery and purification of the small amounts of desired products from the relatively large amounts of unreacted hydrocarbons and the water present a formidable problem, expecially with the higher hydrocarbons.

At pressures up to 100 atmos. and in the temperature range of 250 to 373°C. (482 to 703°F.) with ratios of 1:20 to 1:0.5 propane to air, oxidation of propane results in formation of isopropyl alcohol and acetone (indicating oxygen attack at the β-carbon atom) and considerable proportions of *n*-propyl, ethyl, and methyl alcohols (indicating oxygen attack at the end of the molecule).[1] The higher pressures were found to favor the formation of higher alcohols.

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[1] Pichler and Reder; *Z. angew. Chem.*, **46**, 161–165 (1933).

[2] Newitt and Black, *Proc. Roy. Soc.* (*London*), **A140**, 426, 439 (1933).

TABLE II.—PRESSURE OXIDATION OF ETHANE

Ethane-oxygen mixtures	1	2	3	4
Volume % oxygen in mixture	10	11.8	15.5	11.6
Initial pressure, atmos.	100	100	100	15
Initial temp., °C.	272	262.2	271.8	315
Duration of run, min.	8.75	40.0	......	3.0
% of C in reacted ethane appearing as				
Ethanol	36.5	22.6	7.4	16.0
Methanol	20.0	10.5	10.0	19.4
Acetaldehyde	8.0	6.2	4.8	1.9
Formaldehyde	0.3	0.04	0.9	4.5
Acetic acid	6.5	27.2	2.4	0
Formic acid	0.4	0.8	0.15	0
Total condensed product	71.7	67.34	25.65	41.8

Whole of free oxygen consumed at expiration of run. Remainder of C from ethane appeared as CO, CO_2, and sometimes CH_4 in the gaseous product.

Results from the oxidation of propane and *n*-butane with elemental oxygen at pressures of 130 to 170 atmos. and temperatures of 280 to 350°C. show that more than 40 per cent of the oxygen may appear in the form of liquid organic products.[2] Thus, representative yields from flow experiments are as shown in Table III.

TABLE III.—PRESSURE OXIDATION OF HYDROCARBONS

Oxygen converted to	Oxygen converted, %		
	Propane, 170 atmos. 350°C., 7.9% inlet O_2	*n*-Butane, 140 atmos. 281°C., 6.4% inlet O_2	*n*-Butane, 33 atmos.
Formaldehyde Acetaldehyde	9.4	16.4	6.9
Acetone	2.3	....	1.4
Methyl alcohol	13.4	3.1	15.0
Ethyl alcohol	8.0	6.2	2.5
Propyl alcohol	5.2	9.3	3.2
Butyl alcohol	0.7	1.0	0.6
Acetic acid Formic acid	4.1	11.2	16.7

The composition of the product, as reported, indicates that the tendency is for the formation of alcohols with one or two carbon atoms less per molecule than the parent hydrocarbon. The lower pressures also favor the formation of greater proportions of the lower alcohols and of acids.

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[1] NEWITT and SCHMIDT, *J. Chem. Soc.*, **1937**, 1665–1669.

[2] WIEZEVICH and FROLICH, *Ind. Eng. Chem.*, **26**, 267 (1934).

Pressure oxidation of the heptanes and hexanes results in the formation of still more complex mixtures containing high proportions of alcohols. Recirculation of the oxidized product results in the formation of high proportions of organic acids.

These results teach that elevated pressures are extremely useful in controlling and tempering the oxidation reaction between molecular oxygen and low-molecular-weight hydrocarbons. Even so, it is necessary to use a limited supply of oxygen and to depend upon recirculation of the hydrocarbon in order to obtain high over-all conversions to useful products. Oxygen concentrations of the order of only 5 to 15 mole per cent are used in the feed mixture; and although oxygen conversions of upward of 40 per cent are obtained, the per-pass conversions of hydrocarbon to oxygenated product are not high, and recirculation of unreacted hydrocarbon is essential.

In practically all the patented processes, low concentrations of oxygen, based on the hydrocarbon, are mentioned as desirable.[1] Methods proposed for obtaining these desired low concentrations and for preventing high oxygen ratios due to failure of equipment or control have been based on the solution of oxygen and nitrogen from high-pressure air in the liquid hydrocarbons at room temperature.

The wide variety of catalysts that have been claimed for the pressure-oxidation process throws doubt on the real necessity for having a specific catalyst present in order to obtain the desired reaction rates. It seems that the chief function of the catalyst is to distribute and help dissipate the heat generated by the reaction and to prevent localized high temperatures, which would jeopardize the continued existence of the desired intermediate oxidation products. By employing a divided metal of high heat conductivity, such as copper wire or turnings, and by coating it with some substance to prevent catalysis of decomposition reactions, which are induced by some metals, the desired end would be attained.

On the basis of the foregoing, general deductions relating to the operating conditions may be made as follows: The higher the pressure at which oxidation occurs the higher will be the conversion to alcohols and the lower the conversion to aldehydes, acids, water, and carbon oxides. It is not to be expected, however, that the increase in yield of intermediate oxidation products will be a linear function of the pressure, since other factors are of comparable importance to pressure. A high rate of flow, *i.e.*, high surface velocity over the catalyst, is conducive to the formation of higher alcohols; and a low rate of flow leads to the formation of larger proportions of water, carbon oxides, lower alcohols, aldehydes, and acids. With other conditions fixed, an increase in temperature causes an increase in the secondary reactions, with a consequent decrease in the conversion to higher alcohols. Also, an increase in the concentration of oxygen permits operating temperatures from 100 to 160°C. in liquid-phase processes in which air or gaseous oxygen is contacted with the liquid hydrocarbon. Interest in such oxidations has centered quite largely in the formation of fatty acids, usually hydroxy or aldehydic in nature, suitable for the production of soaps, fats, esters, solvents, etc., or capable of reduction to alcohols for use in manufacture of surface-active agents.

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[1] See Lewis and Frolich, U. S. 1,976,790 (1934); Burke, U. S. 1,978,621 (1934); Burke, Fryling, and Schumann, *Ind. Eng. Chem.*, **24**, 804–811 (1932); Pugh, Taugh, and Warren, U. S. 1,812,714 (1931).

Oxidation of Low-molecular-weight Olefin Hydrocarbons.—Lenher has shown that the slow noncatalytic oxidation of ethylene at temperatures of 400 to 600°C. results in the formation of ethylene oxide and formaldehyde as the major products.[1] The formation of a peroxide or addition complex was postulated as the initial step, which is followed by a stepwise sequence of consecutive reactions leading in the end to the formation of water and oxides of carbon. With elevated pressures, oxidation of ethylene occurs at much lower temperatures. Oxidation of ethylene with air in mixtures having the composition 2 parts of ethylene and 1 part of air starts at a temperature of about 150°C., when the pressure is initially 50 atmos. at room temperature.[2] Under these conditions but at a reaction temperature of 200°C., about 18.5 per cent of the inlet oxygen appears in the product as organic acids, and smaller amounts as alcohols. Practically all the alcohol fraction is reported to be methanol under these conditions. However, a small conversion to ethanol is claimed.

At high propylene and low oxygen concentrations and at reactor temperatures of 500 to 600°C., the noncatalytic, thermal reaction of propylene and oxygen results in pyrolysis as well as oxidation of the olefin, the products of oxidation from experiments in which the unreacted gases have been recirculated consisting of acetaldehyde, formaldehyde, formic acid, carbon oxides, and water. Concomitant pyrolysis results first in the formation of higher monoolefins, which react further to form hydrogen, paraffins, and unsaturated hydrocarbons.

The process for the catalytic oxidation of ethylene to ethylene oxide based on the invention of Lefort has been practiced commercially on a large scale.[3] Ethylene oxide has become an important organic chemical, being used in the manufacture of ethanolamines, β-phenylethyl alcohol, plastics, plasticizers, resins, insecticides, coolants, surface-active agents, solvents, explosives, etc.

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[1] Lenher, *J. Am. Chem. Soc.*, **53**, 3737, 3752 (1931).

[2] Pichler and Reder, *loc. cit.*

[3] Lefort, U. S. 1,998,878 (1935); Reissue 20,370 (1937); Reissue 22,241 (1942).

Although many materials have been tested and patented as catalysts for the direct oxidation of ethylene to ethylene oxide, silver supported on some form of inert material seems to be the best so far developed. The Lefort patent discloses catalysts of silver alone; silver activated with small amounts of iron, copper, or gold; mixtures of silver, antimony, and bismuth; and mixtures of silver and bismuth. The introduction of water or hydrogen along with the ethylene-oxygen (air) mixture is claimed to reduce the amount of oxidation leading to wasteful formation of CO_2. Operating temperatures in the range of 150 to 400°C. and pressures above atmospheric are shown.

One of the improvements on the Lefort process has been based on the introduction of an "anticatalyst" to repress the amount of complete oxidation of ethylene to CO_2.[1] The more important of these are volatile halogen-containing compounds, of which ethylene dichloride is an example. When added in the ratio of 0.02 part by weight per part of ethylene to the reaction mixture, ethylene dichloride is described as acting so as to direct the reaction of ethylene 60 per cent to ethylene oxide and 40 per cent to CO_2 and water at 290 to 300°C. over a barium oxide-promoted, silver catalyst.

Very limited data are available from the literature on the circumstances of the process.[2] The paper by McBee *et al.* gives data from runs with a silver oxide-coated corundum catalyst and on the effect of ethylene dichloride used as an anticatalyst. A temperature of about 268°C. was found best for fresh catalysts and somewhat higher for used catalysts, with air-ethylene volume ratios of 10.5:1 and a contact time of about 1 sec. The conversions of reacting ethylene to ethylene oxide were about 55 per cent with fresh catalyst and about 45 per cent with month-old catalyst. The addition of small amounts of ethylene dichloride had the effect of reactivating the used catalyst with respect to rate of ethylene oxide formation. Large ratios of air to ethylene gave the best results under a variety of conditions.

Various other oxides of vinyl compounds have become commercially available, notably propylene oxide, butadiene monoxide, and styrene oxide.

The conversion of olefins to alcohols via aldehydes by reaction with

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[1] Law and Chitwood, U. S. 2,279,469; 2,279,470 (1942); Berl, U. S. 2,270,780 (1942); McNamee and Blair, U. S. 2,238,474 (1941); National Research Council of Canada, *Chem. Ind.*, **56**, No. 2, 242 (1944).

[2] REYERSON and OPPENHEIMER, *J. Phys. Chem.*, **48**, 290 (1944); REYERSON and SWEARINGEN, *J. Am. Chem. Soc.*, **50**, 2872 (1928); McBEE, HASS, and WISEMAN, *Ind. Eng. Chem.*, **37**, 432 (1945); TWIGG, *Trans. Faraday Soc.*, **42**, 284–291 (1946).

H_2—CO mixtures at high pressures has been claimed to occur under a variety of conditions of catalysts and temperatures.[1] The so-called "OXO process" was practiced in Germany during the Second World War for the production of high-molecular-weight alcohols, C_{12} to C_{18}, which were used in the manufacture of synthetic detergents. Application of the process to low-molecular-weight olefins, such as C_3 and C_4 for the formation of C_4 and C_5 alcohols was apparently carried only through the experimental stage in Germany.[2]

The increasing technical importance of maleic anhydride has stimulated interest in its production by direct oxidation of aliphatic hydrocarbons. Vapor-phase oxidation of olefins in the presence of vanadium pentoxide catalysts results in substantial yields of maleic anhydride which increase with increase in molecular weight of the olefin. Thus, from pentene-2, trimethylethylene, tech. amylene, methyl pentene, heptene, and octene, approximate relative conversions of 10, 25, 27, and 30 per cent, respectively, were obtained from 5, 6, 7, and 8 C-atom olefins.[3] Optimum temperatures of about 425°C. were found for amylene oxidation. Catalysts used for 250 hr. showed no reduction in activity.

The effect of halogenation of paraffin hydrocarbons is comparable with that of unsaturation with respect to catalytic oxidation to maleic anhydride or fumaric acid.[4] Thus, in the presence of vanadium oxides supported on Alfrax pellets or pelleted aluminum turnings, such halogenated hydrocarbons as *n*-butyl chloride, *n*-butyl bromide, 1, 2-dichlorobutane, mixed amyl chlorides, dichlorpentane, polychlorpentanes, *n*-hexyl chloride, and chlorinated kerosene yield varying amounts of maleic anhydride (fumaric acid). With commercial dichloropentane at 425 to 450°C. and a space velocity of 50 reciprocal hours, a conversion of 0.35 mole fumaric acid and 1.88 moles HCl per mole of dichlorpentane was obtained. From 2-chlorobutene-2 at 375°C. over a tin vanadate-molybdenum catalyst, Finch and Evans obtained a 7.9 mole per cent yield of fumaric acid.

Oxidation of Liquid Petroleum Hydrocarbons.—Vapor-phase oxidation of hydrocarbons with molecular oxygen has been applied to compounds that are liquid under ordinary conditions and that have a molecular weight corresponding to the kerosene and gas-oil fractions. To make possible the use of temperatures for oxidation that are sufficiently low to prevent complicating cracking and decomposition reactions in this latter process, it has been found expedient to use certain fixed oxidation catalysts.

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[1] Roelen, U. S. 2,327,066 (1944).

[2] Reference should be made to documents relating to investigations in Germany of the Technical Industrial Intelligence Division made available by the Publications Board, Department of Commerce; T.O.M. Rept. No. 44.

[3] Faith and Dendurent, *Refiner*, **18,** No. 10, 61–64 (1939).

[4] Faith, *Ind. Eng. Chem.*, **37,** 438 (1945); Finch and Evans, U. S. 2,358,775 (1944); Faith, U. S. 2,365,631 (1944).

The James process (Fig. 6) has been directed principally to the vapor-phase, catalytic oxidation of kerosene, although heavier fractions have been processed by the method.[1] The apparatus consists of a device for vaporizing the hydrocarbon, a reactor containing the catalysts and provided with inlets for oxygen or air, and finally a cooling and collection system. The oil vapors pass through a succession of thin catalyst screens, and fresh air in controlled quantities is added to the vapor stream before the first and each succeeding catalyst screen. In this way, air is admitted at each point only sufficient to maintain the catalyst screens at the operating temperature of 350 to 400°C. for kerosene.

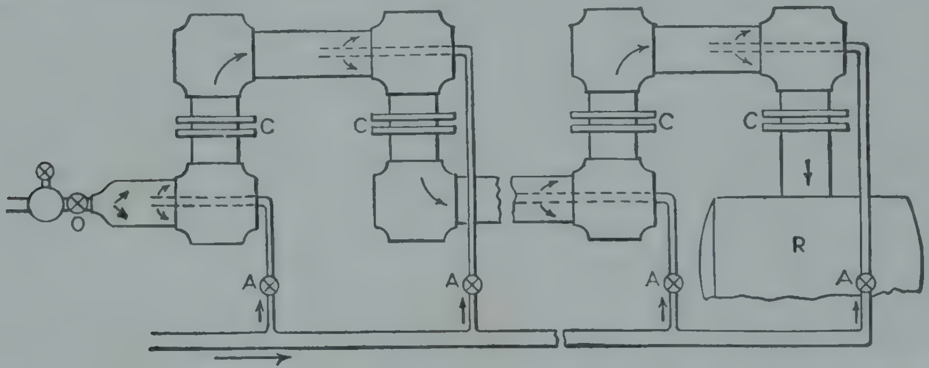

Fig. 6.—Type of apparatus used for oxidation of mineral oils by James process.

A. Air control valves.
C. Catalyst screens.
O. Oil control valve.
R. Product receiver.

The oxides of certain metals of high atomic weight and low atomic volume, such as molybdenum and uranium, have been found to act as useful catalysts in the process. Salts such as diuranyl vanadate have also been found to give good results. The catalyst is arranged in the form of multiple screens which may all be alike or contain different oxides. Temperature control is obtained by regulation of the rate at which oil vapors pass through the apparatus, of the proportion of air or oxygen admitted between catalyst screens, and in the loss of heat from the surface of the tubular chambers. Vapor-phase catalysts such as tetraethyl lead and nitric acid give product mixtures similar to these screen catalysts.[2]

The products from the oxidation of such mixtures of hydrocarbons as are contained in kerosene or gas oil are very complex—so much so as to defy accurate analysis. They contain aldehydes, alcohols, ketones, acids, ethers, and esters. In the oxidation of kerosene, the oxidized oil may be as high as 40 per cent of the total and consist of 30 to 40 per cent of mixed aldehydes, 40 to 45 per cent of mixed alcohols,5 per cent of free acids, 10 per cent of esters, and some ethers. About 85 per cent recovery is claimed with kerosene. With heavy oils, recovery is said to reach 92 per cent. By oxidizing naphtha, kerosene, and wax distillate, lacquer solvents comprising mixtures of esters, alcohols, and ethers may be obtained. The acids—generally aldehydic or aldehydic-hydroxy in type—are difficult to free of complex aldehydes, which impart objectionable odors and resinous polymerization products to soaps formed by saponification of the acid fraction with hot alkali. Methods involving the intermediate formation of calcium soaps have been proposed to avoid the inclusion of aldehydic bodies in the alkali soaps. Sulfonation of the oxidized product leads to the formation of emulsifying agents and "activators" for emulsified insecticides.

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[1] James, *Trans. Am. Inst. Chem. Eng.*, **14,** 189–199 (1921); **14,** 201–210 (1922); *Chem. Met. Eng.*, **26,** 209–212 (1922); Bitler and James, *Trans. Am. Inst. Chem. Eng.*, **20,** 95–100 (1927).

[2] Parks and Story, *Oil Gas J.*, **39,** 54, 56, 58, 61 (1940).

VI. VAPOR-PHASE OXIDATION OF AROMATIC HYDROCARBONS

The aromatic hydrocarbons are characterized by offering several points of resistance to further oxidation or decomposition during the course of the interaction with oxygen, making possible the isolation of intermediate oxidation products. For instance, in the case of naphthalene oxidation, the interaction of 3 atoms of oxygen results in the formation of α-naphthoquinone—a point of resistance since appreciable quantities of this compound may be obtained under the proper conditions. The interaction of a total of 9 oxygen atoms results in the formation of phthalic anhydride. Another resistance point occurs after the reaction of 18 oxygen atoms when maleic anhydride is formed. Thus, it is possible to obtain commercial yields of phthalic anhydride from naphthalene, maleic anhydride from benzene, anthraquinone from anthracene, etc. Because of the thermal stability and resistance to oxidation of the aromatic hydrocarbons and the intermediate reaction products, it is necessary to employ excess oxygen, operate at elevated temperatures, and make use of active catalysts. These factors make it possible to conduct the oxidation so as to obtain commercial yields at practically complete reaction of raw material with only a single pass over the catalyst.

Oxidation of hydrocarbons containing an aromatic nucleus and one or more aliphatic side chains may be effected in the side chain. The side chains behave, in general, like aliphatic hydrocarbons and, as such, are more susceptible to attack by oxygen than the ring. Indeed, it is possible to effect oxidation of the side chains of alkylated aromatic hydrocarbons without ring rupture by the use of air or oxygen under pressure in a noncatalytic liquid-phase reaction.[1] At atmospheric pressure, the principal point of resistance in such oxidized compounds is the aromatic acid formed after oxidation has reached and affected the last carbon atom attached to the nucleus. Unless low concentrations of oxygen are used or mild conditions imposed, this resistance point is the first one to be effective. Thus, ethyl-benzene is oxidized to benzoic acid just as toluene is.[1] The ring structure is so stable toward oxidation or dissociation that regardless of the length of side chains, carboxylic acids result before ring rupture occurs. Under special conditions, such as elevated pressures (50 atmos.) and mild temperatures (210°C., 410°F.), it has been shown that hydroxylated derivatives such as benzyl alcohol and products from oxidation of the aromatic nucleus such as dihydroxy toluene may be recovered.[2] The relatively greater ease of oxidation of the aliphatic side chains makes unnecessary and undesirable the high ratios of oxygen to hydrocarbon used in the oxidation of naphthalene to phthalic anhydride or of benzene to maleic anhydride. Although the reaction is highly exothermic, less heat is evolved per pound of benzaldehyde formed from toluene than per pound of phthalic anhydride from naphthalene, the proportion being of the order of 1545 to 5460 B.t.u., respectively. This ratio for the case of benzoic acid production is 2310 B.t.u. relative to 5460 B.t.u.

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[1] Forrest and Frolich, U. S. 1,902,550; 1,936,427 (1933). This process is unique also in that temperature control is effected by control of pressure on the reactants and heat removal is effected by refluxing of the reacting hydrocarbon.

Noncatalytic oxidation of the aromatic hydrocarbons is slow at temperatures below 500°C. Benzene is not vigorously oxidized in glass chambers until temperatures near 700°C. are attained. Under similar conditions, toluene is noticeably oxidized at 650°C., and xylene at 575°C.[3] Even with an active catalyst such as vanadium pentoxide, a temperature of 400 to 450°C. is required for the industrial oxidation of naphthalene to phthalic anhydride with air. Furthermore, quantities of air from one to three times that theoretically necessary for the conversion must be used. This means that 20 to 60 moles of air must be used per mole of naphthalene introduced to the oxidation chamber for oxidation to phthalic anhydride.

Benzene.—Benzene presents a very stable configuration toward both thermal dissociation and oxidation. The primary effect of exposure of benzene to elevated temperatures is the dissociation of a hydrogen atom accompanied by the joining of the residues to form diphenyl, a more stable substance which may be recovered in good yield. Vapor-phase oxidation to phenol is possible and has been attained with comparatively low yields and conversions. However, phenol does not present any great stability toward oxidation, and its commercial production by this method is somewhat limited at the present stage of development. Continued oxidation results in the formation of quinol and quinone, both of which have been identified in the vapor-phase oxidation products of benzene. High yields have not been obtained, however, owing, no doubt, to the comparative instability of the ring at this stage of oxidation. Continued oxidation results in rupture of the ring and leads to the formation of maleic acid, which may be obtained in good yields. The complete combustion of benzene thus probably involves the formation of quinone and maleic acid as the main points of stability before complete combustion products are reached.

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[1] MAXTED, *J Soc. Chem. Ind.*, **47,** 101–105T (1928).

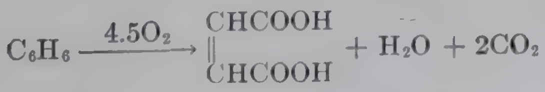
[2] NEWITT and SZEGO, *J. Soc. Chem. Ind.*, **52,** 645 (1933); BONE, *ibid.*, **53,** 963 (1934).

[3] MARDLES, *Trans. Faraday Soc.*, **27,** 681 (1931).

Limited commercial adaptation of a noncatalytic vapor-phase process for oxidation of benzene to phenol has occurred.[1] Practice of the process has shown that one of the main difficulties lies in the control of the reaction to prevent excessive production of diphenyl on the one hand and gaseous oxidation products on the other. A large, insulated reaction chamber is used, and a preheated mixture of benzene vapor and air is allowed to react in the empty chamber. The preferred volume (molal) ratio of air to benzene is in the range of 0.5:1.5; a suitable reaction condition is at 450°C., 8 atmos., and a reaction time of 230 sec. A certain interdependence between pressure and temperature is noted in that the lower the pressure the higher must be the reaction temperature. Conversions of benzene reacted to phenol as high as 50 per cent are reported when the per-pass conversions were from 4 to 8 per cent of theoretical based on benzene fed. Preferred operation is such that formation of gaseous by-products is at a minimum. The presence of gaseous iodine is claimed to improve the process.[2]

Maleic anhydride, maleic acid, and its isomeric form fumaric acid have become increasingly important in the production of resins and plastics.[3] Various esters and condensation products are being made and developed. Maleic acid may be converted to malic acid by heating in aqueous solution under pressure, and the malic acid can be used in place of citric and tartaric acids as an organic acidulant. Succinic acid, derived by reduction, is being used in the manufacture of certain resins, plastics, and plasticizers.

The commercial production of maleic acid by oxidation of benzene has, in a large measure, been due to the early work of Weiss and Downs on



$$C_6H_6 \xrightarrow{4.5O_2} \begin{matrix} \text{CHCOOH} \\ \| \\ \text{CHCOOH} \end{matrix} + H_2O + 2CO_2$$

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[1] Moyer and Klingelhoefer, U. S. 2,223,383 (1940); Porter, U. S. 2,382,944 (1945).

[2] Horman, U. S. 2,382,148 (1945).

[3] See CAROTHERS, *Chem. Rev.*, **8,** 361 (1931); DOWNS, *Ind. Eng. Chem.*, **26,** 17–20 (1934); MARK and WHITBY (Editors) "Collected Papers of Wallace Hume Carothers on High Polymers," Interscience Publishers, Inc., New York, 1940.

this particular reaction and of Gibbs and his associates at the Bureau of Chemistry in Washington on aromatic oxidations in general.[1]

The stability of benzene and the fact that 9 atoms of oxygen are required for the oxidation of a molecule of benzene to maleic anhydride necessitate the use of high air-to-hydrocarbon ratios in the oxidation. Thus, the theoretical requirement would be about 106 cu. ft. of dry air at room temperature per pound of benzene oxidized to maleic anhydride. In practice, higher ratios than this are used, and yields of 60 to 75 lb. of maleic acid per 100 lb. of benzene reacted are obtained. This represents an efficiency of conversion of benzene to maleic acid of about 40 to 50 per cent.

The heat theoretically liberated in the oxidation of benzene to maleic acid is about 10,500 B.t.u. per pound of benzene reacting, and the heat liberated in the complete combustion of benzene is approximately 18,000 B.t.u. per lb. In practice, where 40 per cent or more of the benzene may undergo complete combustion during reaction, the heat liberated would be 13,500 B.t.u. or more per pound of benzene reacted. It is imperative that this reaction heat be removed from the catalyst zone and that the catalyst temperature be maintained at the proper operating level. Special means have been provided for this in commercial operation.

A variety of catalysts have been patented for this oxidation, and the oxides of metals of the fifth and sixth groups of the periodic system have been particularly stressed. Of these, vanadium pentoxide has been shown to be one of the best when used as a single-component catalyst supported on an inert carrier such as aluminum turnings or diatomaceous earth. Mixtures of vanadium with other oxides of these groups have been patented, and a variety of multicomponent zeolitic mixtures claimed. Vanadium pentoxide becomes active in promoting the oxidation at a temperature of about 300°C. and reaches its maximum usefulness in the range of 400 to 500°C. Data on the other catalysts are not available.

The exhaust vapors from the manufacture of phthalic anhydride by the vapor-phase, catalytic oxidation of naphthalene carry considerable quantities of maleic acid. The application of proper recovery methods to these exhaust gases has made them an industrial source.

Toluene.—The oxidation of hydrocarbons having an aromatic nucleus and one or more side chains may be effected in the side chain without marked rupture of the ring itself, since each component behaves more or less as it would if it alone constituted the major part of the molecule. Thus, the ring component exhibits the characteristic stability of the aromatic compounds, and the aliphatic substituent shows the relatively greater ease of oxidation of the aliphatic hydrocarbons. Under specific conditions, oxidation of such substituted aromatic hydrocarbons may be controlled to give satisfactory yields of the side-chain products; *viz.*, toluene may be oxidized to benzaldehyde or benzoic acid; *o*-xylene, to phthalic anhydride; ethylbenzene, to benzoic acid; etc.

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[1] Weiss and Downs, *Ind. Eng. Chem.*, **12**, 228 (1920); *J. Am. Chem. Soc.*, **45**, 1003, 2341 (1923); *J. Soc. Chem. Ind.*, **45T**, 193 (1926); Weiss, Downs, and Burns, *Ind. Eng. Chem.*, **15**, 965 (1923); Weiss, Downs, and Corson, *ibid.*, **15**, 628 (1923).

Considerable benzoic acid is manufactured by the decarboxylation of phthalic acid, a process that yields a chlorine-free product. The development of this decarboxylation process has served to restrict the investigation of air-oxidation methods.

The products of toluene oxidation, chiefly benzaldehyde, benzoic acid, maleic acid, and anthraquinone, are obtained in proportions that depend upon catalyst, temperature, oxygen ratio, and time of contact. High temperatures, mild catalysts, and short times of contact promote the formation of benzaldehyde. High oxygen ratios and long times of contact, are, in general, conducive to acid formation. At temperatures of 280 to 300°C., reaction begins in the presence of vanadium oxide catalysts, but reaction is slow; long times of contact are required, and benzoic acid tends to be the major product. At temperatures of 400 to 450°C., reaction becomes more rapid over the vanadium oxide catalysts, and benzaldehyde, representing about 50 per cent of the toluene oxidized, becomes the principal product. Molybdenum oxide is a milder catalyst, and a temperature of 450 to 530°C. is necessary for good per-pass yields and high conversion to benzaldehyde. In the temperature range of 420 to 450°C. and in the presence of vanadium oxide catalysts, as much as 5 per cent of the reacted toluene may appear in the product as anthraquinone. At temperatures above 500°C. in the presence of molybdenum

TABLE IV.—VAPOR-PHASE OXIDATION OF TOLUENE[1]

Catalyst of Tin Vanadate. Toluene Carbureter Temperature, 40°C.; Catalyst Temperature, 290°C.

Space velocity of		Vol. of air per vol. of toluene vapor[2]	Yield benzoic acid, %	Space-time yields of acid[3]
Primary air[4]	Secondary air			
200	500	40.8	53.3	0.020
200	700	52.5	41.0	0.0112
200	1,000	70.0	36.3	0.0135
300	2,000	88.6	32.9	0.0137
300	3,000	128.6	23.8	0.0105

[1] MAXTED, *J. Soc. Chem. Ind.*, **47**, 101–105T (1928).

[2] Calculated on basis of saturation of air by toluene vapor in carbureter.

[3] Space-time yield $= \frac{\text{gm. of product}}{\text{(hr.) (cc. of catalyst space)}}$.

[4] Primary air is the air admitted directly with the hydrocarbon; secondary air is subsequently admitted to this primary mixture.

oxide catalysts, considerable proportions of the reacted toluene may appear in the product as a complex, high-boiling oil. The results of oxidations with tin vanadate as a catalyst are given in Table IV.

Oxidation of toluene with large excesses of air over an alumina (Alfrax) supported vanadium oxide catalyst has been claimed to be an effective method for benzoic acid production.[1] Thus, the use of air to toluene weight ratios of 39 to 49:1, temperatures on the order of 410 to 430°C., and contact times of 0.25 to 0.75 sec. are claimed to result in yields of benzoic acid of about 34 per cent with corresponding maleic acid yields of 7 to 11 per cent based on toluene consumed in the process.

Ethyl Benzene.—The dehydrogenation of ethyl benzene to styrene may be facilitated by the addition of oxygen (air) to a steam-ethylbenzene vapor mixture undergoing dehydrogenation.[2] The added oxygen "burns off" hydrogen, furnishing exothermic heat of reaction. Substantial quantities of benzoic acid have been made as a by-product of this process in connection with the large-scale production of styrene for the synthetic rubber program.[3]

Xylene.—As a result of the huge, wartime expansion of toluene production by the petroleum-refining industry, the xylenes have become available in quantities potentially far exceeding that formerly available from the coke-oven by-product industry.

The proportions of the isomers present in coal tar xylenes are about 15 per cent ortho, 15 per cent para, and 70 per cent meta. The proportions of the isomers from the petroleum processing may vary somewhat depending upon the source of the crude but approximate 25 to 30 per cent ortho, 20 ± per cent para, 40 to 50 per cent meta, plus some ethyl benzene.

Ortho xylene is readily separated from the mixture by fractional distillation and may be oxidized to phthalic anhydride by processes similar to those used with naphthalene. Already one plant, using *o*-xylene and having a design capacity for 7,000,000 lb. of phthalic anhydride annually, is in commercial operation in California. As the demand for phthalic anhydride increases in the face of limited quantities of naphthalene, further production from *o*-xylene may be expected.

Since the oxidation of *o*-xylene to phthalic anhydride requires the theoretical interaction of only 6 atoms of oxygen relative to the 9 required by naphthalene, the amount of heat generated per unit of product is less, making the process easier to control. Some commercial operating details are now available.[4] Favorable factors are low air ratios and low CO_2 formation. Both of these factors tend to facilitate product recovery by reducing the proportions of diluent gases. Also product purification should be easier because of the decreased formation of quinones and color bodies.

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[1] Parks and Yula, U. S. 2,289,036 (1942).

[2] Natta, U. S. 2,308,229 (1943).

[3] Stanley, *Chem. Ind.*, **1938,** 93.

[4] *Chem. Ind.*, July, 1946, p. 68–69; *Chem. Met. Eng.*, **53**, 116 (1946).

Catalytic vapor-phase oxidation of *m*-xylene results in formation of maleic anhydride in yields comparable to those obtained from benzene, *e.g.*, about 40 to 50 per cent of theoretical. Relative to benzene, *m*-xylene requires more oxidation to convert it to maleic anhydride and, under the present circumstances, is a relatively more expensive raw material.

Naphthalene.—In point of volume and importance to the dye and synthetic organic chemical industries, the oxidation of naphthalene to phthalic anhydride is without peer among the various processes involving aromatic hydrocarbon oxidation. Since the development of the catalytic vapor-phase oxidation process, the price of phthalic anhydride has dropped steadily and the volume of production has risen rapidly. The present price is about 13 cts. per lb. and the volume of production in 1944 was approximately 120 million pounds.[1]

Phthalic anhydride is the raw material for the manufacture of anthraquinone and a number of its derivatives by the Friedel-Crafts' reaction. In this way, it finds extensive use in the manufacture of the important vat intermediates and dyes, such as alizarin and alizarin derivatives. It is used for the fluorescein, eosine, and rhodamine dyes. Phthalate esters are widely used in the lacquer industry as plasticizers. Reacted with glycerol, phthalic anhydride forms the glyptal and rezyl types of resins which find extensive commercial use. The manufacture of phenolphthalein and that of chloride-free benzoic acid are additional outlets for phthalic anhydride. During the war, over 90 per cent of production was used in the manufacture of esters and synthetic resins. The use of dimethyl phthalate as an insect repellent accounted for substantial proportions of that used in ester production.

The stability of the naphthalene structure is such that at temperatures up to 400 or 500°C., a catalyst is necessary for commercial rates of oxidation with air as the oxidizing agent. The first point of resistance to continued oxidation is marked by the formation of α-naphthoquinone, which may be obtained as a product of the oxidation by suitable regulation of conditions. For instance, the controlled oxidation of naphthalene with chromic acid in acetic acid solution may be made to yield α-naphthoquinone. In vapor-phase oxidation of naphthalene with a catalyst of 10 per cent vanadium pentoxide on pumice, a ratio of air to naphthalene about the theoretical required for oxidation to phthalic anhydride, and a temperature of about 400°C., the oxidation of naphthalene has been qualitatively shown to lead to the formation of naphthoquinones.

The next stable product of the oxidation is phthalic anhydride, which is generally the intermediate desired from naphthalene oxidation. Continued reaction, however, may lead to benzoic acid formation by the splitting off of carbon dioxide from the phthalic anhydride. Continued oxidation accompanied by ruptures of the benzene ring results in the formation of maleic anhydride. In the industrial production of phthalic anhydride, quantities of maleic anhydride are formed and pass out with the exhaust gases from the condenser system. Further oxygen attack leads to the complete combustion of the products or at least to the formation of small amounts of formaldehyde with the complete combustion products. Thus, the principal steps in naphthalene oxidation are the addition of oxygen to the naphthalene ring, the destruction of the naphthalene ring, and the destruction of the remaining benzene ring.

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[1] Department of Commerce, *Ind. Ref. Ser.*, vol. 3, Pt. 2, No. 17, May, 1945.

Theoretically, 9 atoms of oxygen are required per molecule of naphthalene for oxidation to phthalic anhydride. This means that 64.5 cu. ft. of dry air measured at room temperature is theoretically required for the oxidation of 1 lb. of naphthalene to phthalic anhydride. In practice, considerable excess air is used, up to three times that theoretically required. Thus, from 20 to 60 moles of air must be used per mole of naphthalene oxidized.

The heat of oxidation theoretically amounts to 5460 B.t.u. per pound of naphthalene oxidized. Owing to the fact that some complete combustion also occurs, the heat actually liberated amounts more nearly to 10,000 B.t.u. per pound of naphthalene oxidized. Specially designed catalyst chambers must be used to remove this heat without disturbing the temperature equilibrium of the catalyst mass.

Catalysts similar to those mentioned for benzene oxidation are applicable to the naphthalene reaction. The early work and published results have shown that vanadium and molybdenum oxides are effective and quite active catalysts. With supported vanadium pentoxide catalysts, commercial conversions of naphthalene to phthalic anhydride in excess of 80 per cent of theoretical are obtained. Such catalysts have a long life—6 months or more of continuous use—and have yielded up to twenty thousand times their weight of phthalic anhydride.[1] Fused or supported vanadium pentoxide catalysts become active for the oxidation at temperatures of 270 to 280°C. and induce reaction at commercial rates at temperatures of near 400°C. Although pumice, crushed to size, was formerly used as a support for the vanadium catalysts, the poor heat-conducting capacity of this porous medium and the tendency for the metal oxide to react with the support have led to adaption of other materials. Infusorial earth formed into pellets either before or after impregnation with the metal salt of the catalyst forms an inert support but has poor heat-conducting capacity. Aluminum turnings with rough surfaces form a good support, being inert and having good heat-conducting characteristics.

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[1] Downs, *J. Soc. Chem. Ind.*, **45**, 188T (1926).

It has been claimed that mixtures of the metal oxides form better catalysts than the oxides alone. For instance, a mixture of 85 per cent of vanadium pentoxide with 15 per cent of molybdenum oxide is claimed to be better than the vanadium oxide alone; and a mixture of 65 per cent vanadium pentoxide, 30 per cent of molybdenum oxide, and 5 per cent either manganese or calcium oxide, still better.[1]

Published data show that certain salts of the catalytically active metals are effective. The vanadates of tin and bismuth are effective catalysts for the oxidation and, on a laboratory scale, permit yields of over 80 per cent in one pass of the reacting mixture over the catalyst.[2] Tin vanadate is effective in the temperature range of 250 to 320°C. when very high air ratios and space velocities[3] of 2,300 to 6,200 are used. The bismuth vanadate catalysts require considerably higher temperatures for the effective oxidation of naphthalene.

Many other catalysts have been tried and patented. Among the reputedly more useful of these are the zeolitic or base-exchanging types of siliceous and nonsiliceous compounds. The majority of these zeolitic combinations which have been proposed contain such catalytically active elements as vanadium, molybdenum, tungsten, chromium, uranium, copper, and nickel.

For the recovery of phthalic anhydride from the hot, dilute mixture of gases and vapors issuing from the catalytic converter, the normal technic is to effect condensation of the phthalic anhydride in large, roomlike cooling chambers (indicated in Fig. 9) where the product deposits in the form of a bulky mass of long, needlelike crystals.

To reduce the space required for this recovery, to improve the density and control the purity, and to reduce the amount of manual labor required, it has been proposed to accomplish recovery by use of a sequence of steps: (1) Cool the vaporous mixture by passage through a water-cooled tubular cooler-condenser; (2) remove the bulk of the condensed material by means of a scraper-screw conveyer in the cold end of this cooler; and (3) recover dust from the cold gases by means of a bag filter.[4]

VII. APPARATUS FOR OXIDATIONS

Liquid-phase Reactions.—Liquid-phase reactions in which oxidation is secured by the use of oxidizing compounds need no special apparatus in the sense that elaborate means must be provided for temperature control and heat removal. There is usually provided a kettle form of apparatus, closed to prevent the loss of volatile materials and fitted with a reflux condenser to return vaporized materials to the reaction zone, provided with suitable means for adding reactants rapidly or slowly as may be required and for removing the product, and provided with adequate jackets or coils through which heating or cooling means may be circulated as required. Examples of such apparatus are scattered throughout this book, and no specific examples are required here.

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[1] Craver, U. S. 1,489,741 (1924); see Wohl, U. S. 1,971,888 (1934). for other catalyst compositions.

[2] Maxted, *J. Soc. Chem. Ind.*, **47,** 191–195T (1928).

[3] Space velocity is expressed as volumes of gas measured at normal temperature and pressure passed per volume of catalyst per hour.

[4] Riegler, U. S. 2,067,019 (1937).

In the case of liquid-phase reactions in which oxidation is secured by means of atmospheric oxygen, for example, the oxidation of liquid hydrocarbons to fatty acids, special means must be provided to secure adequate mixing and contact of the two immiscible phases of gaseous oxidizing agent and the liquid being oxidized. Although temperature must be controlled and heat removed, the requirements are not severe, since the temperatures are generally low and the rate of heat generation controllable by regulation of the rate of air admission. All these factors are important, and the apparatus must provide for them.

Figures 1, 2, and 3 show how, in general, this may be accomplished. Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid and constructed of materials capable of withstanding temperatures that may be considerably higher at these inlet ports than in the main body of the liquid. With materials that are sensitive to overoxidation and under conditions where good contact must be used partly to offset the retarding effect of necessarily low temperatures, thorough mixing may be provided by the use of mechanical stirring or frothing of the liquid.

THE PROBLEM OF HEAT TRANSFER IN VAPOR-PHASE REACTIONS

By their very nature, the vapor-phase oxidation processes result in the concentration of reaction heat in the catalyst zone from which it must be removed in large quantities at high-temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material, and maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation. With laboratory-scale apparatus, removal of this heat is relatively easy; in some instances, it is even necessary to provide an external supply of heat in order to maintain the operating temperature at the proper level. With plant-scale operation and with reactions involving deep-seated oxidation, removal of heat constitutes a major problem. With limited oxidation, however, it may become necessary to supply heat even to oxidations conducted on a plant scale.

In the case of vapor-phase oxidation of aliphatic substances such as methanol and the lower molecular-weight aliphatic hydrocarbons, the ratio of reacting oxygen is generally lower than in the case of the aromatic hydrocarbons for the formation of the desired products, and for this reason heat removal is simpler. Furthermore, in the case of the hydrocarbons, the proportion of oxygen in the reaction mixture is generally low, resulting in low per-pass conversions and in some instances, necessitating preliminary heating of the reactants to reaction temperature. Figure 4 shows a schematic layout for the oxidation of methanol to formaldehyde. Figures 5 and 6 show apparatus for the oxidation of hydrocarbons.

Rather elaborate means have been perfected for the oxidation of the aromatic hydrocarbons to useful compounds. Such apparatus must be designed to permit the maintenance of constant elevated temperatures, to permit the removal of large quantities of heat at these elevated temperatures, and to provide adequate catalyst surface to promote the reactions. One form of converter adapted to accomplish these ends consists of numerous small catalyst tubes immersed in a liquid bath.[1] The liquid bath may be used to remove heat from the reaction as latent heat of evaporation of the liquid; it may be subjected to forced circulation in contact with the catalyst tubes and cooled in an external heat exchanger; or it may be used as a means of getting reaction heat to an outer retaining shell from which the heat is dissipated to the atmosphere.

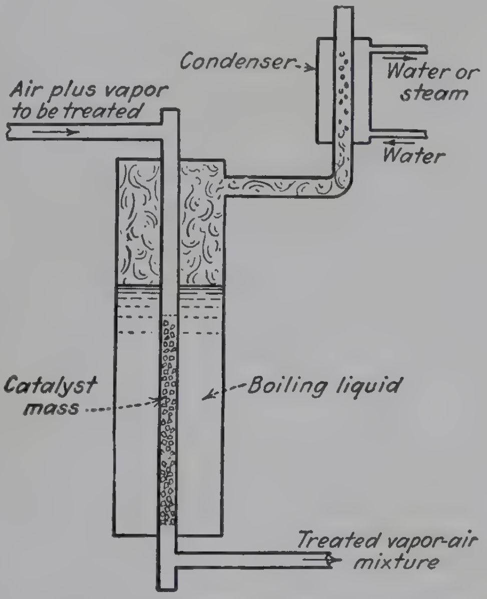

FIG. 7.—Section of single-tube reactor with boiling-liquid heat removal and temperature control.

Figure 7 is a diagrammatic section of a single-tube reactor and shows the principles involved in the removal of reaction heat as heat of evaporation and the dissipation of this heat to cooling water. The entering air-hydrocarbon (naphthalene) mixture first comes in heat-transferring contact with the heated vapors of the boiling liquid and is thus preheated before coming in direct contact with the catalyst. Cooling of the first section of the catalyst is thus avoided to a certain extent, and the catalyst mass is made more effective in promoting the reaction. Reaction heat, liberated at the catalyst surface, passes from the catalyst mass through the tube wall and to the surrounding liquid, where it is removed at constant temperature by the evaporization of the liquid. The evolved vapors from the bath may be condensed in a separate condenser provided with cooling water, and the condensed material returned to the bath. Continuous operation is thus obtained. In practice, it is customary to use a large number of such tubular catalyst chambers in parallel, connected at the top and bottom by common headers. Such a converter is largely automatic in operation and does not depend upon atmospheric conditions for satisfactory operation. As shown in Fig. 8, a suitable air- and water-cooled condensing system returns the mercury to the liquid reservoir and removes the heat of reaction thereby. The mercury (liquid and vapor) is thus the means for removing the heat of a reaction at a constant temperature of about 425°C. and for dissipating it to cooling water at a temperature of about 100°C. Heat is thus effectively removed without affecting the temperature of the catalyst adversely.

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[1] DOWNS, *J. Soc. Chem. Ind.*, **45,** 188–193T (1926); U. S. 1,374,020; 1,374,021 (1921); 1,604,739 (1926); Canon and Andrews, U. S. 1,614,185 (1927); Reissue 16,824 (1927).

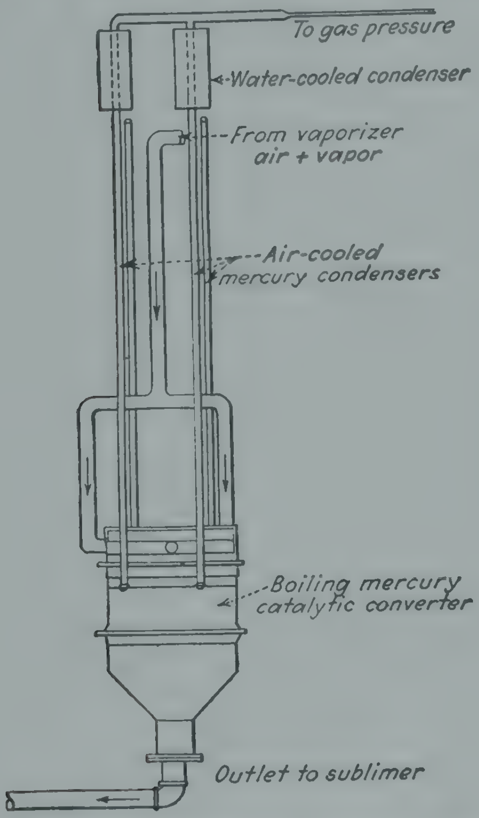
To gas pressure
Water-cooled condenser
From vaporizer air + vapor
Air-cooled mercury condensers
Boiling mercury catalytic converter
Outlet to sublimer

FIG. 8.—Multiple-tube converter using two-phase mercury system.

By varying the pressure on the two-phase mercury system it is possible to control the temperature of the liquid bath and of the catalyst mass. This may be accomplished by the use of nitrogen pressure. Also the boiling point of the mercury can be altered by introducing alloying metals such as cadmium.

The capacity of such a converter is from 1,500 to 1,800 lb. (816.5 kg.) or even more of phthalic anhydride per 24 hr., depending upon catalyst activity, rate of feed, etc. Production at this rate means the generation of large quantities of heat in the converter. Although the heat of oxidation of naphthalene to phthalic anhydride is about 6000 B.t.u. per pound (3330 cal. per kg.) of naphthalene, the occurrence of a certain amount of complete combustion during the oxidation reaction brings the heat evolution up to approximately 10,000 B.t.u. per pound (5550 cal.

per kg.) of naphthalene fed to the converter. About 21,000,000 B.t.u. (5,300,000 cal.) is generated per day and removed by the boiling mercury and as sensible heat in the hot exit products during operation on the above basis.

Mercury has both advantages and disadvantages for use as the heat-removing fluid. Its boiling point of 357°C. at atmospheric pressure may be easily raised to 400 to 450°C. by the application of nitrogen pressure. It is fluid at room temperature and introduces no hazard of equipment damage due to solidification through accidental cooling because of shut-down of equipment. Latent heat of evaporation at 357°C. is 117 B.t.u. per lb. (65 cal. per kg.). Mercury vapor is toxic; the liquid is heavy; and leaks in the pressure system are difficult to prevent. These last factors, together with cost, operate as disadvantages. Some of these objectionable features have been overcome in practice. Proper construction and design have reduced mercury loss by leakage to about 1 per cent per year. Mercury has a low coefficient of thermal conductivity and does not wet the steel-tube walls. However, the violent motion given to the mercury by its own boiling tends to counteract these effects. Other materials, fluid at operating temperatures, have been proposed as superior to mercury in some respects. Among them sulfur, diphenyl, diphenyl oxide, and mercury amalgams may be mentioned here.

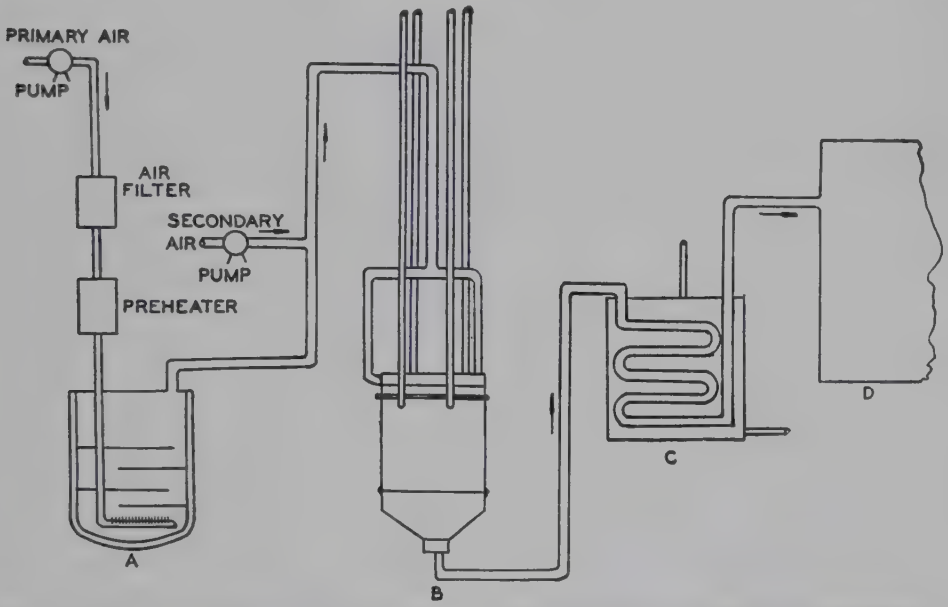

FIG. 9.—Schematic layout for oxidation of naphthalene to phthalic anhydride.

A. Vaporizer for naphthalene.
B. Converter for oxidation reaction.
C. Cooler.
D. Condenser for phthalic anhydride.

The method of removing heat of reaction from the reaction zone by the evaporation of a liquid from a bath, as embodied in the process described above, has been uniquely modified by Forrest and Frolich in such a way that the liquid being oxidized also provides the means for heat removal and temperature control.[1] Cyclic organic compounds are oxidized directly with molecular oxygen by contacting them with an oxygen-containing gas, such as air, in a closed system at an elevated temperature and under a pressure substantially greater than the vapor pressure of the compound at the reaction temperature. The closed system contains a condenser directly communicating with the liquid being oxidized and, by means of the circulation of a cooling medium there through the mixture of gases and vapors rising from the liquid, is cooled, and the vapors condensed and returned to the liquid batch undergoing oxidation. Air is forced in at the bottom of the liquid through a distributor head, and the noncondensable gases, *i.e.*, unreacted oxygen, nitrogen, and reaction products, are vented at a point above the condenser through a pressure-regulating valve. The temperature of operation must be below the critical of the compound being treated, but it has been found that this condition is easily satisfied. There have been no indications that this process has been reduced to commercial practice.

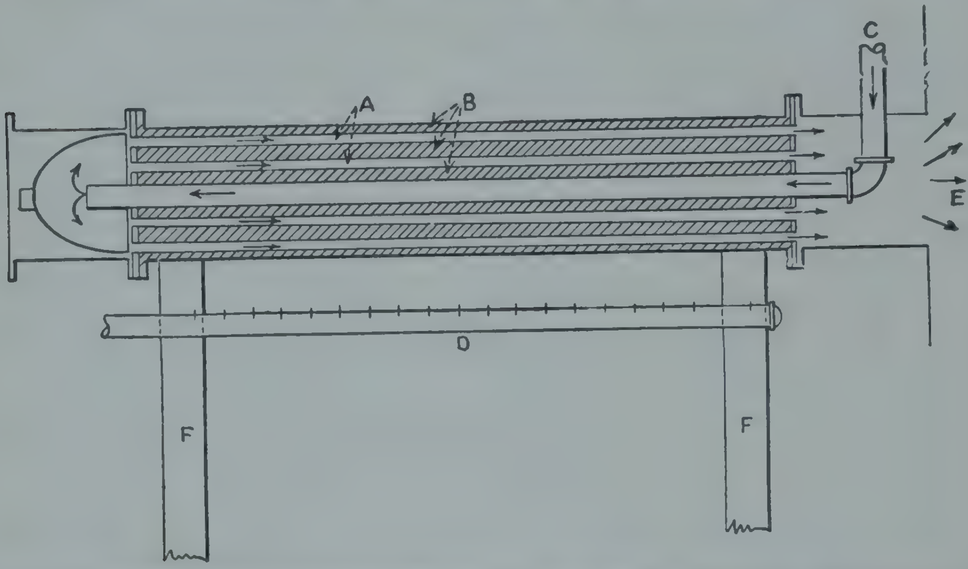

FIG. 10.—Catalytic multiple-tube converter for oxidation reaction with heat removal from surface of shell to atmosphere.

A. Tubes containing catalyst.
B. Heat-conducting medium.
C. Inlet for air and vapors.
D. Gas burners for starting.
E. Condenser.
F. Supports.

Instead of removing reaction heat by evaporation, the liquid surrounding a batch of catalyst tubes may serve simply as a means of heat transfer. Thus, Fig. 10 shows a method of removing heat from the surface of a retaining shell by releasing it to the atmosphere. Either forced or natural circulation of the fluid may be used to convey the heat from the catalyst tubes to the point of disposal. Fluids of low vapor pressures are preferable in such methods, and fused salts such as potassium-sodium nitrate mixtures may be used.

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[1] Forrest and Frolich, U. S. 1,902,550 (1933).

The fluid catalyst or jiggling process, developed in recent years for catalytic cracking of petroleum in gasoline production, has been adapted for the oxidation of naphthalene to phthalic anhydride.[1] A plant designed for 2,500,000 to 3,000,000 lb. of phthalic anhydride annually gave yields of 75 lb. phthalic anhydride of 99 per cent purity per 100 lb. of 169 to 170°F. melting point naphthalene after the first month of operation. Air from reciprocating compressors is passed through preheaters and into the 5 ft. diameter by 30 ft. tall reactor containing the powdered catalyst. Melted naphthalene is sprayed into the reactor at the rate of 400 lb. per hr., vaporizes, and mixes with the air therein. Some of the powdered catalyst passes out with the product stream and is removed by cyclones and filters. Phthalic anhydride is recovered in condensers. The tail gases are scrubbed and passed to the air. Advantages claimed are higher purity of product, lower air ratio, less explosion hazard, less labor, outdoor equipment, and lower operating temperatures.

[1] LEE, *Chem. Met. Eng.*, **52,** No. 7, 100–101 (1945).

CHAPTER VIII

HYDROGENATION

By Merrell R. Fenske

I. INTRODUCTION

Types of Reduction.—Reduction is the term usually applied to a reaction in which oxygen is withdrawn from or hydrogen added to a compound. In addition, other elements besides oxygen may be eliminated from a molecule by the action of hydrogen, the most common being nitrogen, sulfur, carbon, and halogens. In these cases, ammonia, hydrogen sulfide, methane, and the hydrogen halides are usually formed. Reduction may be performed in a variety of ways: (1) by metals in acid or basic solutions; (2) by alkali metals in alcoholic solutions; (3) by electrolysis; and (4) by molecular hydrogen and catalysts. Catalytic reduction by hydrogen is one of the most common and important methods from a commercial point of view, and the discussion here is confined to this one. Technical applications of other methods appear in Chap. II.

In order to correlate and condense the innumerable and diversified examples of catalytic hydrogenation, the following arbitrary classification has been made. This involves only the four type reactions:

1. Reduction of an ethylenic linkage:

$$R{\cdot}CH{:}CHR' + H_2 \rightarrow R{\cdot}CH_2{\cdot}CH_2R'$$

where R and R′ are aliphatic or aromatic groups.

2. Reduction of a carbonyl to an alcohol group; or to a hydrocarbon:

$$CO + 2H_2 \rightarrow CH_3OH$$
$$R{\cdot}CH_2{\cdot}CO{\cdot}R' + H_2 \rightarrow R{\cdot}CH_2{\cdot}CHOH{\cdot}R'$$

or

$$xCO + yH_2 \rightarrow \text{hydrocarbons} + \text{water (or carbon dioxide)}$$

where R is an aliphatic or aromatic group, and R′ is the same or a hydrogen atom.

3. Reduction of a carboxyl to an alcohol group:

$$R{\cdot}COO{\cdot}R' + 2H_2 \rightarrow RCH_2OH + R'OH$$

where R is preferably an aliphatic or hydroaromatic group, and R′ is the same or a hydrogen atom.

4. Hydrogenolysis, or reactions involving molecular cleavage on the addition of hydrogen.

Survey of Technical Hydrogenations.—Hydrogenation processes have been steadily increasing in size, variety, and importance, and the unit process of hydrogenation is becoming one of the most useful and widespread in organic synthesis. The earliest technical application of hydrogenation was practically limited to the reduction of the double bond between two carbon atoms for the purpose of converting liquid fats into solid fats, or, as it is often called, fat hardening. This industry is now well established. It is estimated that the annual production of hydrogenated fats is about 750,000 tons in the United States.

The fats resulting from the hardening of whale oil, fish oil and the vegetable oils such as linseed, soybean, and cottonseed oil, by the addition of hydrogen under pressure, are of two types—edible and nonedible. The edible fats are used as lard, butter substitutes, and shortening compositions in the baking industry and for the manufacture of creams and coatings for confections. The soap industry is the largest consumer of nonedible hardened oils. Other minor uses for the nonedible products are in leather dressings, electrical insulations, candlemaking, paint manufacture, and pharmaceutical ointments.

Another development of importance to the soap industry is the manufacture of sulfuric acid esters of long-chain aliphatic alcohols such as lauryl, cetyl, and stearyl alcohols. Instead of making the sodium salt of palmitic or stearic acid, as in ordinary soap manufacture, these acids are first reduced to the corresponding alcohols by hydrogenation at high pressure, and the alcohols then esterified with sulfuric acid. These detergents, which are used in the form of the sodium salt, have some very interesting properties; thus, they are equally soluble in hard or soft water. They are well suited for hard waters, and their emulsifying and wetting powers are better than ordinary soaps. Whereas ordinary soaps in acid media are decomposed into fatty acids that are difficultly removed, particularly from fine fabrics, the sodium palmityl and stearyl sulfates are soluble in acid, neutral, or alkaline media without decomposition into insoluble compounds. Fatty acids either may interfere with dyeing operations or later may become rancid and give off disagreeable odors. The sulfuric acid esters do not become rancid and, because of their high solubility, are easily and completely washed out of fabrics. These detergents, although more expensive than the ordinary soap, will find many applications in washing fine fabrics and fibers, in toilet preparations, and wherever their advantages more than offset their higher price.

Commercial production of synthetic methanol and higher alcohols in this country dates from about 1925. In the year 1944 about 71,000,000 gal. of methanol was made by direct synthesis from water gas in the United States. A large variety of organic chemicals can be made from water gas, or high-pressure hydrogenation of carbon monoxide. It is also possible to make a variety of hydrocarbon mixtures suitable as motor fuels by the catalytic hydrogenation of carbon monoxide. Whereas the

United States has extensive petroleum resources which furnish these hydrocarbons at present at lower cost, those countries which have coal rather than petroleum reserves are now in a position to synthesize their liquid fuels in this manner from the cheap raw materials—coal, water, and air. This country has large reserves of natural gas, and there is an increasing incentive to transform this into liquid fuels. One way of doing this is to convert the gas to a carbon monoxide-hydrogen mixture from which liquid hydrocarbons can be synthesized. Important developments of this type are in progress.

The hydrogenation of petroleum, coals, and tar not only offers conservation of the petroleum supply but also makes available the enormous reserves of coal for the production of liquid fuels. Petroleum hydrogenation is being carried out in the United States, and coal hydrogenation in Germany and England, and such hydrogenations are necessarily large-scale operations. During the war, a large part of Germany's liquid fuels was prepared by the high-pressure hydrogenation of coal, tar, and lignite and by the catalytic reduction of carbon monoxide by the Fischer-Tropsch synthesis, using cobalt-type catalysts and pressures in the range of 1 to 10 atmos. at about 180 to 220°C. It is estimated that nearly a million tons of liquid fuel were produced in Germany in 1940 by the Fischer process. If the energy content of the liquid fuel is referred to that of the coal needed to prepare it, it appears, with the Fischer-Tropsch process for hydrogenation of carbon monoxide, that about 30 per cent of the energy of the coal is available as the liquid fuel whereas, in the direct hydrogenation of coal, from 30 to 40 per cent of the heat energy of the coal is available as a liquid fuel.[1] Thus these processes appear to be the answer to a possible dwindling supply of natural petroleum.

Naphthalene and phenolic oils which are obtained from coal tar are produced in excess in some countries. Hydrogenation of naphthalene gives two liquid solvents—tetralin, which results when 4 atoms of hydrogen are added, and decalin, when 10 atoms are added. Hexalin, or cyclohexanol, and the ketone cyclohexanone are the products resulting from hydrogenating phenol; and methylhexalin, the product resulting from hydrogenating cresols. These hydrogenated materials, either alone or when mixed with each other, are important solvents for camphor, fats, oils, waxes, natural and synthetic resins, and rubber. They also find application in a variety of special soaps and detergents, for they are valuable emulsifying and solubilizing agents for soaps and oils.

Thus far, only a few applications of hydrogenation to the production of foodstuffs, detergents, chemicals, and fuels have been indicated. There is a long list of applications in the field of synthetic organic chemistry relating to the reduction of all types of unsaturation such as olefinic,

[1] SCHLATTMANN and KOPPENGER, *Nat. Petroleum News*, **28**, No. 37, 24E (1936).

aldehydic, nitro, and nitrogen linkages. The applications are constantly changing and increasing in number; such is always the case in any active field of endeavor.

There are, however, certain lines of research upon which the future of hydrogenation will be dependent: (1) a better understanding of the processes and of other physical factors affecting hydrogenation, together with additional knowledge concerning the chemical reactions occuring; (2) an extension of the knowledge of catalysis; and (3) the development of cheaper hydrogen. The following summary pertains to the problem of hydrogen and its production in quantity.

II. PRODUCTION OF HYDROGEN

In the development and operation of processes involving reduction by means of hydrogenation, the problem of the hydrogen supply is important. In the small-scale or research phase of the problem, hydrogen is readily available in cylinders and is usually of sufficient purity so that at this stage of the development work, no thought need be given to the hydrogen supply. However, as soon as semiplant or commercial operation of the process begins, not only the problems of hydrogen production but also those of purification, handling, storage, and compression appear. Sometimes, these seem to outweigh all the earlier problems concerned with getting the desired reaction to proceed.

The first need for hydrogen on a relatively large scale resulted from the introduction of lighter-than-air craft and from the development of the process for hydrogenation of vegetable oils—the so-called fat-hardening industry.

The synthetic ammonia process has steadily expanded. The synthesis of methanol and other alcohols, and the hydrogenation of mineral oils, tars, and coals have also progressed. The manufacture of hydrocodimer or technical isooctanes, an important component of high antiknock aviation fuel, developed remarkably during the war. Hydrocodimer consists of a mixture of isomeric octanes boiling in the range of about 100 to 115°C. Thus, surprisingly large quantities of hydrogen are needed by only a relatively few processes, as is evidenced by the following Table I.

TABLE I.—ESTIMATED HYDROGEN CONSUMPTION IN THE UNITED STATES IN 1944 FOR AMMONIA, METHANOL, AND HYDROCODIMER

Product	Hydrogen Consumed, Billion Cu. Ft.
Synthetic ammonia (production, over 1,000,000 tons)	70.0
Synthetic methanol (production, 71,000,000 gal.)	10.5
Hydrocodimer (production, 150,000,000 gal.)	2.7

During the first 9 months in 1944, the gasworks in England supplied supplied 0.4 billion cubic feet of hydrogen for barrage balloons used in air defenses against aircraft, flying bombs, and rockets.

It is estimated that the chemical and petroleum processing plants consumed about 24 billion cubic feet of hydrogen in 1944.

Upon cheap hydrogen in large quantities will depend the expansion of the present processes as well as the creation of new ones. Following are the most important methods available at the present time for hydrogen production.

Hydrogen from Water Gas and Steam.—The water-gas catalytic, or Bosch, process is one of the most important for producing industrial hydrogen today. Water gas is readily made in standard water-gas generators from very cheap raw materials, *viz.*, coal or coke, steam, and air. An average analysis of water gas is

Hydrogen	49.2%
Carbon monoxide	41.3%
Carbon dioxide	4.2%
Oxygen	0.2%
Methane	0.8%
Nitrogen	4.3%

The carbon monoxide in the gas is made to react with steam in the presence of a catalyst, and additional hydrogen along with carbon dioxide is obtained.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The result of this reaction is that the water gas is converted essentially into a gas composed of carbon dioxide and hydrogen. The carbon dioxide is easily removed by scrubbing with water under pressure or by other absorbents such as triethanolamine, leaving a gas composed essentially of hydrogen (see Appendix 6). If necessary, it is purified further to remove the small amounts of the other gases. For example, small amounts of carbon monoxide are removed by scrubbing with ammoniacal solutions of copper salts.

The water-gas catalytic process is usually carried out at about 450 to 500°C. (840 to 930°F.) and generally at substantially atmospheric pressure. The reaction is exothermic, so once it is started it is self-supporting. Although there are many catalysts that may be used, they generally consist of oxides of iron promoted by chromium oxide, cobalt oxide, and alumina. The reaction is reversible, so that if the temperature is too high, the conversion is not complete. It can be forced to greater conversion, however, by using an excess of steam, which is usually the practice. The steam is easily condensed and so removed from the gases as they are cooled.

These gases, containing 60 to 80 per cent hydrogen, 20 to 40 per cent carbon dioxide, less than 1 per cent carbon monoxide, and smaller amounts of other gases, are then usually stored in gas holders. They are taken as needed from the holders to the compressors, for the hydrogen is practically always used at elevated pressure. At some intermediate stage in the compression, where the pressure may be from 250 to 1,000 lb. per sq. in., the mixture of gases is led from the compressors to the scrubbing towers where the carbon dioxide is removed, after which the gas goes back to the compressors to be compressed to the final working pressure. The water–gas–steam process is usually employed where high-pressure hydrogen is needed and is perhaps one of the cheapest methods for large-scale continuous production of hydrogen. The method is used in the synthesis of ammonia, methanol, and higher alcohols and in manufacturing motor fuels by the hydrogenation of coals or tars.

Hydrogen from Water Gas or Coke-oven Gas by Liquefaction.—This is a physical process of purification based on the difference in boiling points of the components of the gas when liquefied. It has developed through the work of Claude, Patart, and the Linde Company. It is not extensively used in this country, for the water-gas catalytic process appears more economical. The gas, after being freed from tar, ammonia, benzene, and sulfur in conventional ways, is scrubbed at high pressure with water and caustic. It is freed of water by cooling with ammonia to about −45°C., after which it goes to the liquefaction and fractionation apparatus, where the process is similar to the separation of nitrogen and oxygen from air.[1] Coke-oven gas, because of its nitrogen content, is usually worked up for ammonia synthesis, whereas water gas is more suitable for the production of hydrogen alone. Coke-oven gas may contain about 50 per cent hydrogen and some 15 to 20 per cent nitrogen, together with 20 to 30 per cent methane, unsaturated hydrocarbons, and carbon monoxide. The hydrogen produced in this process can undoubtedly be made very pure.

Hydrogen from Hydrocarbons.—Hydrogen may be prepared from hydrocarbons by two processes: (1) thermal decomposition and (2) reaction with steam. The first of these reactions involves the complete decomposition, or cracking, of natural gas into carbon and hydrogen. At present, gases high in methane are cracked to produce carbon black by the thermatomic-carbon process. The hydrogen is a by-product and is used principally for fuel.

The second process is becoming increasingly important. It is undoubtedly the best method available for petroleum hydrogenation or synthesis plants to produce hydrogen from natural gas, from waste refinery gas, or from the gaseous products resulting from hydrogenation. These gases are composed principally of methane, and the reaction with steam is

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[1] Pallemaerts, *Ind. Eng. Chem.*, **21**, 22 (1929); *Intern. Conf. Bituminous Coal*, II. 212 (1929).

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

This is a catalytic reaction and occurs at about 1000°C. (1800°F.) in special furnaces. The catalyst is an aluminum oxide base in the form of small pellets or cubes. The reaction is quite highly endothermic, and so the catalyst is contained in tubes consisting of a high-chromium, high-nickel alloy steel capable of withstanding these high temperatures. The waste heat in the flue gas from the furnaces is utilized by means of waste-heat boilers to produce about half the steam required in the process.

More steam is added to the carbon monoxide-hydrogen mixture, and the water-gas catalytic reaction is then made to take place over an iron-base catalyst at 450 to 500°C. (840 to 930°F.). The gases leaving this converter contain about 79 per cent hydrogen, 20 per cent carbon dioxide, and 1 per cent unconverted hydrocarbons and miscellaneous gases. They are cooled and scrubbed to remove the carbon dioxide, just as in the water-gas catalytic process.

The reaction of hydrocarbons and steam is thus a continuous process, capable of making available the large quantities of combined hydrogen existing in natural and refinery gases principally as methane, ethane, and some unsaturated hydrocarbons. This reaction is used in the petroleum hydrogenation plants in this country and will probably be employed extensively in other hydrogenation and synthesis plants where large quantities of similar gases are available.

A modification of the above process consists of employing hydrocarbon gases and oxygen with steam and probably some carbon dioxide to produce directly a carbon monoxide-hydrogen mixture for hydrocarbon synthesis by the Fischer process.

Hydrogen by Electrolysis of Water.—Cheap electrical power is the principal factor determining the production of hydrogen by the electrolysis of water. The purity of this hydrogen is an asset. By-product hydrogen from electrolytic chlorine-alkali processes is available, for instance, at Niagara Falls, where it is used for ammonia synthesis. This method of hydrogen production is perhaps the best available for small plants where the operations are not large enough to warrant the large-scale water-gas catalytic method of production. Such plants generally use hydrogen in various syntheses or in the preparation of organic chemicals. Even though the cost of hydrogen by electrolysis is more than by other methods, it is a convenient and workable method for plant work on a small scale.

Hydrogen from Steam and Iron.—The principal reactions for the production of hydrogen from steam and iron are

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2 \qquad (1)$$

$$\left\{\begin{array}{l} Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O \\ Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2 \end{array}\right\} \qquad (2)$$

The reaction is intermittent, the iron being oxidized to produce the hydrogen and then regenerated as indicated by reactions (2) by passing water gas over it.[1] This method has been used for some time and is adapted to small- or moderate-scale operations. However, it is gradually being supplanted by other methods of hydrogen production. The production of hydrogen from steam and iron has been extensively used in the past in connection with hardening or hydrogenation of vegetable oils. Because of the relative simplicity of such installations, the bulk of the hydrogen for barrage balloons over England during the war was made by the steam-iron process.

Properties of Hydrogen.—Apart from the more commonly known physical and chemical properties of hydrogen are a few that are of primary importance in the handling and use of hydrogen and hydrogenation equipment. Because it is the lightest gas, it will diffuse or leak where other heavier gases will not, particularly at high pressure. It is usually more difficult to have gastight connections and fittings when working with hydrogen than with other gases such as air or steam. Particular attention should be given to all fittings, valves, and connections that are to be used on hydrogen. A leak not only means a loss of hydrogen but is, in addition, a decided hazard due to the inflammability and very wide explosive limits that hydrogen possesses. These limits are much wider than for most gases, as Table II shows.

These data show that a relatively small leakage of hydrogen or any carelessness in allowing air to mix with hydrogen might be dangerous.

TABLE II.—EXPLOSIVE LIMITS OF GASES[1]
Per Cent by Volume in Air

Gas or vapor	Percentage of gas	Gas or vapor	Percentage of gas
Hydrogen	4.15 to 75.0	Ethylene	3.2 to 34.0
Carbon monoxide	12.5 to 75.0	Propylene	2.2 to 9.7
Methane	4.9 to 15.4	Acetylene	1.5 to 80.5
Ethane	2.5 to 15.0	Benzene	1.4 to 8.0
Propane	2.2 to 7.3	Toluene	1.3 to 6.8

[1] YEAW, *Ind. Eng. Chem.*, **21**, 1030 (1929).

Adding 4.15 per cent or more of hydrogen to air or 25 per cent or more air to hydrogen results in explosive mixtures. Too much care cannot be exercised in designing and operating equipment in which hydrogen is used. All apparatus and lines should be carefully purged by an inert gas such as nitrogen, carbon dioxide, or flue gases not containing oxygen, before hydrogen is admitted.

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[1] ELLIS, "Hydrogenation of Organic Substances," 3d ed., p. 716, D. Van Nostrand Company, Inc., 1930.

Hydrogen at elevated temperatures and pressures in contact with ordinary carbon steels is particularly corrosive. The tensile strength of these carbon steels is due to a particular iron structure and to their carbon content. With iron alone, hydrogen forms a hard, brittle hydride; and with carbon steels, in addition to the embrittling action, it causes trouble by attacking and removing carbon, reducing oxides, and producing cracks and fissures. The effect depends upon the state of the hydrogen, whether atomic or molecular; upon the composition of the metal; and on the temperature and pressure. With embrittlement and the removal of carbon, the tensile strength of the steel is greatly reduced, so that continued use of the apparatus may be dangerous. Special alloy steels are entirely resistant to this hydrogen attack. The attack of hydrogen and hydrogen sulfide on steels has been studied extensively.[1]

Alloy steels are more resistive than carbon steels. Chrome-vanadium, chrome-vanadium-aluminum, chrome-nickel-vanadium-aluminum steels; stainless steels (18 per cent chromium, 8 per cent nickel, or 24 per cent chromium and 20 per cent nickel); and BTG metal (12 per cent chromium, 60 per cent nickel, 2.5 per cent tungsten) have been found to be completely resistant. BTG metal is the special alloy developed for the Claude ammonia synthesis, where operating pressures extend to 15,000 lb. per sq. in. and temperatures to 560°C.

Chromium has been found particularly efficient in preventing penetration and the attack of hydrogen. Chrome-vanadium steels are used frequently, for high-pressure hydrogenation reactors. These steels average about 0.30 per cent carbon, 2 per cent chromium, and 0.02 per cent vanadium. The 18-8 (chromium-nickel) steels are also commonly employed.

Cost of Hydrogen.—Although it is realized that cost estimates are difficult to make and are sometimes unreliable and misleading, the following estimates have been prepared to indicate more particularly the relative proportions of one item to another in making up the total cost of hydrogen. For any plant, the cost of hydrogen will depend on (1) the location and proximity to cheap fuel and power; (2) the size of the plant; (3) the purity of the hydrogen required; (4) the pressure at which it is employed; and (5) the type of process by which it is made. Cost estimates have been made on producing hydrogen from water gas and by electrolysis of water. In either case, the final purity of the hydrogen is very high, the water-gas hydrogen having been purified so that it is substantially equivalent to electrolytic hydrogen in order that the basis for the two may be comparable.

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[1] Cox, *Chem. Met. Eng.*, **40**, 407 (1933); Berthelot, *C. A.*, **33**, 2088 (1939); Puchner, *C. A.*, **37**, 6621 (1943).

For a small water-gas plant, the total cost, excluding the price of water gas, is about 35 cts. per 1,000 cu. ft. of hydrogen at ordinary pressure and temperature. The preparation of hydrogen by reacting the constituent carbon monoxide with steam is about 48 per cent of this cost; the removal of the carbon dioxide by water scrubbing, about 20 per cent; and the final purification, about 32 per cent. When water gas is available at 20 cts. per 1,000 cu. ft., the total cost per 1,000 cu. ft. of hydrogen made from it on a relatively small scale is about 60 cts.

The most important items in making hydrogen by the electrolysis of water are the cost of electric power and the amortization charges. The more expensive type of equipment needed and the charges upon it are reflected in the fact that for a plant producing about a million cubic feet of hydrogen per day by electrolysis, the costs, exclusive of power, are about 40 cts. per 1,000 cu. ft. With power available at 0.5 ct. per kilowatt hour, the total cost of hydrogen is about $1.15 per 1,000 cu. ft., at ordinary temperature and pressure. With power available at 0.25 ct. per kilowatt hour, the price would be about 78 cts. and, at 0.75 ct. per kilowatt hour, about $1.45. In these calculations, no credit was given to the value of the oxygen produced along with the hydrogen; *i.e.*, it was assumed to have no value.

Compressing the hydrogen to 3,000 lb. per sq. in. would cost about 20 cts. per 1,000 cu. ft., if power were available at 1 ct. per kilowatt hour. On this basis, the energy cost would be just about one-half the total cost; fixed charges, labor, maintenance, and repairs account for the other half.

The cost of hydrogen in the large plants hydrogenating petroleum and coal may be very low—from 15 to 30 cts. per 1,000 cu. ft. compressed to 3,500 lb. per sq. in. This is due to the fact that natural gas or waste refinery gases are used, and that in all these plants the cost of power is very low—perhaps 1 mill per kilowatt hour. In these cases, the cost of compression per 1,000 cu. ft. to 3,500 lb. is of the order of 10 cts.

Along with the cost of hydrogen, it is necessary to know the amount consumed in the various processes. For the case of relatively pure or definite chemical compounds, the required amount of hydrogen is readily calculated. In the fat-hardening industry, about 34 cu. ft. of hydrogen is consumed per ton of oil per unit drop in iodine value. For hardening the common oils such as castor, cottonseed, linseed, olive, palm, rapeseed, soybean, sunflower seed, and whale oils, the hydrogen consumption amounts to from 0.8 to 2 cu. ft. per lb.

Thus, in hydrogenating common chemicals, the cost of hydrogen would probably not be more than 1 ct. per pound of material hydrogenated; in the fat-hardening industry, it would be only a few mills per pound of hardened oil. In the petroleum, tar, and coal hydrogenation processes, the cost of hydrogen is from a fraction of a cent to 2 cts. per gallon of finished product. These figures are merely the cost of the hydrogen compressed to the pressure needed, and do not include the operating costs, fixed charges, catalyst costs, etc.

III. TYPE HYDROGENATIONS

Hydrogenation of—C= C— Linkages.

General Reaction.—

$$R{\cdot}CH{:}CH{\cdot}R' + H_2 \rightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}R'$$

where R and R′ are aliphatic or aromatic groups. The hydrogenation of an ethylenic to a paraffinic linkage can be accomplished readily, usually in the presence of a nickel or nickel-containing catalyst and sometimes with platinum or palladium catalysts. In general, the hydrogen pressures need not be high, except when the hydrogenation is slow; then, increased pressure usually speeds up the reaction. Since hydrocarbons are generally more volatile than the ester or acid of the same number of carbon atoms, a considerable number of these hydrogenations take place in the vapor phase simply by the vaporized compound and hydrogen being passed over the catalyst at a suitable temperature. However, it is believed that operation at somewhat lower temperatures, but with increased hydrogen pressures, may be more advantageous when hydrogenation at low pressure and high temperature causes a disruption or breaking of the carbon-to-carbon linkages. Examples of the conversion of an ethylenic to a paraffinic linkage are given in the following paragraphs.

The lower molecular-weight olefins, such as ethylene, propylene, butenes, pentenes, hexenes, and heptenes, are readily hydrogenated to the corresponding paraffin hydrocarbon in the vapor phase by passing the olefin and hydrogen over nickel at atmospheric pressure and 100 to 200°C. Care must be taken to keep the temperature as low as possible and still permit hydrogenation; otherwise, at higher temperatures, side reactions involving cleavages in the hydrocarbon chain will occur. It is also advisable for the same reason to use a considerable excess of hydrogen. Under carefully controlled conditions, the reduction proceeds smoothly and furnishes a convenient method for preparing paraffin hydrocarbons, particularly those of lower molecular weight.

Higher molecular-weight olefins can also be hydrogenated in the vapor phase in the presence of a nickel catalyst if they have sufficient volatility at the temperature for hydrogenation, *viz.,* 150 to 200°C.

Otherwise, the reduction is accomplished in a shaking or stirred autoclave in the liquid phase, and hydrogen pressures, from a few to a hundred atmospheres, may be used. Higher hydrogen pressures generally speed up the reduction and permit lower temperatures for hydrogenation. Both these effects minimize side reactions. The catalysts, usually nickel but also platinum or palladium black or their oxides, are kept suspended in the liquid by the mechanical agitation.

Aromatic hydrocarbons, such as benzene, toluene, and xylenes as well as ethyl-, propyl-, butyl-, and other substituted benzenes, can be reduced to the corresponding hexahydrobenzenes when their vapors are passed along with hydrogen over nickel catalysts maintained at temperatures of from 150 to 200°C. In the case of naphthalene or substituted naphthalenes, the product may be the tetra- or decahydronaphthalene derivative. Atmospheric pressures are usually employed in these vapor-phase hydrogenations, although higher hydrogen partial pressures are also suitable. With more substituent groups or with chains longer than butyl or amyl, secondary decomposition products resulting from cracking or the breaking of carbon-to-carbon linkages in the chain appear. In these cases hydrogenating at lower temperatures but with higher hydrogen pressures and using platinum or nickel catalysts is more practical.

TABLE III.—HYDROGENATION OF AROMATIC COMPOUNDS AT 2 TO 3 ATMOS. HYDROGEN PRESSURE AND 25 TO 30°C. WITH PLATINUM OXIDE CATALYST
50 cc. of Glacial Acetic Acid Used as Solvent

Compound	Amount of substance, gm.	Amount of catalyst, gm.	Time, hr.	Compound obtained
Benzene	15.6	0.2	2.0	Cyclohexane
Toluene	18.4	0.2	2.75	Methylcyclohexane
Ethylbenzene	21.2	0.2	7.5	Ethylcyclohexane
m-Xylene	21.2	0.2	21.5	*m*-Dimethylcyclohexane
Mixed xylenes	21.2	0.2	26.0	Mixed dimethylcyclohexanes
Mesitylene	12	0.2	8.5	Trimethylcyclohexane
Cymene	13.4	0.2	7.5	1-Methyl-4-isopropylcyclohexane
Diphenylmethane	16.8	0.2	7.0	Dicyclohexylmethane
Triphenylmethane[1]	8.74	0.8	48.0	Tricyclohexylmethane
α, α-Diphenylethane	18.2	0.6	26.5	α, α-Dicyclohexylethane
Dibenzyl	18.2	0.6	37.0	α, β-Dicyclohexylethane
Phenylacetic acid	13.6	0.2	5.5	Cyclohexylacetic acid
β-Phenylpropionic acid	15.0	0.2	6.0	β-Cyclohexylpropionic acid

[1] Temperature 60°C., 100 cc. of acetic acid.

Cyclic hydrocarbons, other than five or six carbon rings, are hydrogenated with the opening of the ring or with the formation of five- or six-membered rings. Thus, cyclopropane or trimethylene is readily reduced to propane when passed with hydrogen over nickel at 80 to

180°C. Cyclobutane is hydrogenated at 180°C. to butane[1] in a similar manner, while cyclopentane and cyclohexane are not changed to pentane or hexane. These five- and six-membered rings are very stable and do not undergo any change except the usual degradative decompositions at higher temperatures. However, isomerization of six- to five-membered rings and *vice versa* can occur. Cycloheptane and cyclooctane at 200 to 250°C., when hydrogenated with a nickel catalyst, undergo changes to methyl and dimethyl derivatives of cyclopentane and cyclohexane.[2]

Instead of using nickel and hydrogenating in the gas phase at 150 to 200°C., platinum oxide catalysts in the liquid phase and at lower temperatures (25 to 30°C.) give good results, as is shown in Table III.[3]

Examples of high-pressure hydrogenation of a few simple aromatic hydrocarbons are given in Table IV.[4]

TABLE IV.—HYDROGENATION OF AROMATIC COMPOUNDS AT HIGH PRESSURE

Compound	Temperature, °C.	Pressure, atmos.	Time, min.	Catalyst	Product
Benzene (½ mole)........	160–220	48-100	120	0.08 mole Ni 0.08 mole Cu	100% Cyclohexane
Toluene (½ mole)........	220–300	60–130	135	0.08 mole Ni 0.08 mole Cu	100% Methylcyclohexane
ortho-Xylene (6 moles)....	220	92	150	0.7 mole U.O.P. Ni	100% 1, 2-Dimethylcyclohexane
1, 2, 4-Trimethylbenzene (5 moles).	230	83	150	0.6 mole U.O.P. Ni	100% 1, 2, 4-Trimethylcyclohexane
n-Propylbenzene (5 moles).	200	106	90	0.6 mole U.O.P. Ni	100% *n*-Propylcyclohexane
Para-cymene (3.5 moles)..	210	115	90	0.4 mole U.O.P. Ni	100% para-Menthane
Hydrindene (2.9 moles)....	210	122	60	0.4 mole U.O.P. Ni	100% Hydrindane

The hydrogenation of *ethylenic groups* in alcohols, aldehydes, and ketones differ from those in hydrocarbons in that the conditions of hydrogenation must be milder and better controlled in order to reduce the ethylenic linkage and not the carbonyl groups. In general, the reduction of unsaturated alcohols, aldehydes, or ketones proceeds smoothly either by passing the vapor along with excess hydrogen over nickel catalysts or by hydrogenation in the liquid phase, using hydrogen pressures from 3 to 100 atmos. or more. In this latter case, the catalyst is usually suspended in the liquid.

Table V summarizes the conditions of hydrogenation of a few of the simpler compounds.

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[1] WILLSTÄTTER and BRUCE, *Ber.*, **40**, 3979, 4456 (1907).

[2] WILLSTÄTTER and KAMETAKA, *Ber.*, **41**, 1480 (1908).

[3] ADAMS and MARSHALL, *J. Am. Chem. Soc.*, **50**, 1972 (1928).

[4] HERSH and GRAHAM, Undergraduate theses, Penn. State Coll., 1931; KLAUS, M. S. thesis, Penn. State Coll., 1946.

The hydrogenation of *unsaturated acids and esters* is not particularly adapted to vapor-phase reactions because of their low volatility. In general, most of these reductions are carried out in the liquid phase and at somewhat elevated hydrogen pressures. The types of catalyst employed are very similar to those used in saturating ethylenic linkages in more volatile compounds where a vapor-phase reaction is possible. Table VI summarizes a few typical examples.

TABLE V.—REDUCTION OF ALCOHOLS AND KETONES

Compound	Catalyst	Temperature, °C.	Pressure, atmos.	Phase	Products obtained	Reference
Allyl alcohol	Nickel	130 to 170	1	Vapor	Propyl alcohol	1
Tertiary methylheptenols	Nickel	160 to 170	0.02	Vapor	Tertiary methylheptanols with corresponding hydrocarbon	2
Phorone	Nickel	160 to 170	1	Vapor	Diisobutyl ketone	3
Mesityl oxide	Nickel	185	1	Vapor	2-Methylpentanone-4 methylisobutylcarbinol and 2-methylpentane	4
Mesityl oxide	Colloidal platinum	25	1 to 2	Water solution	2-Methylpentanone-4	5
Dibenzalacetone	Colloidal palladium	25 to 80	2 to 3	Benzene-alcohol solution	Dibenzylacetone	6
Phenol	Nickel	100 to 150	15	Liquid	Cyclohexanol	7
Phenol	Platinum oxide	25 to 50	2 to 3	Alcohol solution	Cyclohexanol	8
Cinnamic alcohol	Platinum black	25	1 to 3	Liquid	Cyclohexylpropanol	9
o-, *m*-, and *p*-Cresols	Nickel	220 to 230	1	Vapor	Methylcyclohexanols	10
Xylenols	Nickel	200	1	Vapor	Dimethylcyclohexanols and dimethylbenzenes	11
α- and β-Naphthols	Nickel	170	1	Vapor	Corresponding decahydronaphthols	12
α- and β-Naphthols	Nickel	250	100	Liquid	Corresponding decahydronaphthols	13
Anthraquinone	Nickel	75	50	Tetralin or decalin solution	Tetrahydroanthraquinone	14

[1] SABATIER, *Compt. rend.*, **144**, 879 (1907).

[2] GRIGNARD, *Bull. soc. chim.*, **43**, 473 (1928).

[3] GRIGNARD, *Bull. soc. chim. Belg.*, **37**, 41 (1928).

[4] SKITA, *Ber.*, **41**, 2938 (1908).

[5] *Ibid.*, **48**, 1494 (1915).

[6] PAAL, *Ber.*, **45**, 2226 (1912).

[7] SABATIER and REID, "Catalysis in Organic Chemistry," p. 216, D. Van Nostrand Company, Inc., New York, 1922.

[8] VOORHEES and ADAMS, *J. Am. Chem. Soc.*, **44**, 1404 (1922).

[9] WASER, *Helvetica Chim. Acta*, **8**, 123 (1925).

[10] SABATIER and MAILHE, *Compt. rend.*, **140**, 350 (1905).

[11] *Ibid.*, **142**, 553 (1906).

[12] LEROUX, *Compt. rend.*, **141**, 953 (1905).

[13] IPATIEV, *Ber.*, **40**, 1281 (1907).

[14] SKITA, *Ber.*, **60**, 2526 (1927).

Hydrogenation of Carbonyl (> C=O) Linkages. *General Reaction.*—$R \cdot CO \cdot R' + H_2 \rightarrow R \cdot CHOH \cdot R'$, where R is an aliphatic or aromatic

TABLE VI.—REDUCTION OF UNSATURATED ESTERS AND ACIDS

Compound	Catalyst	Temperature, °C.	Pressure, atmos.	Phase	Products obtained	Reference
Crotonic acid	Nickel	190	1	Vapor	Butyric acid	1
Crotonic acid	Colloidal palladium	25	1	Liquid	Butyric acid	2
Sorbic acid	Colloidal palladium	25 to 75	1	Liquid	*n*-Valeric acid	3
Oleic acid	Nickel	280 to 300	1	Vapor	Stearic acid	1
Oleic acid	Nickel	250	1 to 10	Liquid	Stearic acid	4
Benzoic acid	Colloidal palladium	25 to 50	2	Acetic acid solution	Hexahydrobenzoic acid	5
Ethyl benzoate	Platinum oxide	25 to 50	2 to 3	Alcohol solution	Ethyl hexahydrobenzoate	6
Cinnamic acid	Nickel	100	15	Amyl alcohol solution	Phenylpropionic acid	7
Cinnamic acid	Nickel	300	100	Liquid	Cyclohexylpropionic acid	8
Cinnamic acid	Copper chromite	175	100 to 150	Liquid	Phenylpropionic acid	9
Phenylethyl acetate	Nickel	180	1	Vapor	Cyclohexylethyl acetate	10

[1] SABATIER and MAILHE, *Ann. chim. phys.* [8], **16,** 73 (1909).
[2] BÖESEKEN, WEIDE, and MOM, *Rec. trav. chim.*, **35,** 269 (1915).
[3] FOKIN, *J. Russ. Phys. Chem. Soc.*, **40,** 276 (1908).
[4] LUSH, *J. Soc. Chem. Ind.*, **42,** 219 T (1923); **43,** 53T (1924); **44,** 129T (1925); **46,** 454T (1927).
[5] SKITA, and MEYER, *Ber.*, **45,** 3589 (1912).
[6] GRAY and MARVEL, *J. Am. Chem. Soc.*, **47,** 2799 (1925).
[7] BROCHET and BAUER, *Bull. soc. chim.* (4) **17,** 50 (1915).
[8] IPATIEV, *J. Russ. Phys. Chem. Soc.*, **41,** 1414 (1909).
[9] ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53,** 1903 (1931).
[10] SABATIER, *Compt. rend.*, **156,** 424 (1913).

group, and R′ may be the same or a hydrogen atom. The carbonyl group in aldehydes, ketones, esters, and acids can be reduced by hydrogen with catalysts either partially, to give a hydroxyl (—OH) group, or entirely, to give a hydrocarbon group ($—CH_2—$ or $—CH_3$). The partial reduction is obviously characterized as a mild hydrogenation, and catalysts in this class are, in general, applicable. Carbon monoxide may be considered the simplest compound containing this group, and its hydrogenation leads to the syntheses of alcohols, ketones, acids, and hydrocarbons, the last containing as high as several hundred carbon atoms[1,2] This is because carbon monoxide, on partial reduction, can yield compounds or molecular fragments, *e.g.*, $> CH_2$, which are capable of undergoing extensive condensation on the same catalysts that effect the initial hydrogenation. Thus, from the simple substances carbon monoxide (and, in some cases, carbon dioxide) and hydrogen, practically unlimited syntheses are possible; the greatest problem associated with these reactions is the separation of individual compounds.

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[1] FISCHER, TROPSCH, and NEDDEN, *Ber.*, **60 B,** 1330–1334 (1927).
[2] PICHLER, *Brennstoff-Chem.*, **19,** 226–230 (1938).

Methane results when carbon monoxide and hydrogen in the proportion of 1:3 are passed over a nickel catalyst at ordinary pressure and temperatures of 200 to 250°C.[1] The reaction is

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O$$

With less hydrogen and at higher temperatures, carbon monoxide reacts according to the following equation to form carbon dioxide, rather than with hydrogen to give methane:

$$2CO \rightleftarrows C + CO_2$$

Consequently, there is carbon deposition on the catalyst and loss in activity. At about 250°C. and with a nickel catalyst, the following reaction takes place when the ratio of hydrogen to carbon monoxide is lower.[2]

$$2CO + 2H_2 \rightleftarrows CO_2 + CH_4$$

Methane also results from the reduction of carbon dioxide by hydrogen, according to the reaction[3]

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$$

This equilibrium has been studied.[4] Using a catalyst consisting of 73 per cent charcoal and 27 per cent nickel, which resulted from carbonizing a mixture of sugar and nickel acetate, the decomposition of carbon monoxide into carbon and carbon dioxide was entirely suppressed and the catalyst maintained its activity for months in producing methane. Ferric oxide, vanadium pentoxide, and cerium oxide are promoters for the nickel-charcoal catalyst. Studies have also been made of the various reactions involved in the reduction of carbon monoxide and dioxide.[5]

Higher hydrocarbons result from the reduction of carbon monoxide by hydrogen at atmospheric or low pressure with cobalt-containing catalysts. Fischer and Tropsch initiated this work in 1926.[6] It may be considered a synthetic petroleum. There are formed light hydrocarbons, such as ethane, propane, butane, pentane, etc., which are present in natural gas and "casing-head" gasoline; a product also is obtained that has a distillation range equivalent to that of gasoline and consists of paraffin hydrocarbons and some olefin hydrocarbons; higher fractions equivalent to kerosene and oily products are also present; and, finally, paraffin waxes of melting points of over 100°C. can be made. There may also be present some oxygenated products, such as alcohols, aldehydes, and ketones.[1]

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[1] SABATIER and SENDERENS, *Compt. rend.*, **134**, 514, 689 (1902).

[2] ARMSTRONG and HILDITCH, *Proc. Roy. Soc.*, **103A**, 25 (1923).

[3] SABATIER and SENDERENS, *loc. cit.*

[4] RANDALL and GERARD, *Ind. Eng. Chem.*, **20**, 1335 (1928).

[5] HIGHTOWER and WHITE, *Ind. Eng. Chem.*, **20**, 10 (1928).

[6] FISCHER and TROPSCH, *Brennstoff-Chem.*, **7**, 97, 299 (1926); *Nat. Petroleum News*, Oct. 13; Oct. 20, 1926.

The catalysts contain iron, nickel, copper, and cobalt along with metallic oxides. Cobalt appears to be the best of the metals, and the oxides of chromium, zinc, rare earths, aluminum, magnesium, and manganese are used. Erdeley and Nash use catalysts of the following combinations: cobalt-copper-aluminum oxide, cobalt-copper-manganese oxide, cobalt-copper-zinc oxide, cobalt-copper-cerium oxide, and cobalt-copper.[2]

In general, the temperature range for the production of these hydrocarbons is between about 200 and 300°C.; much below 200°C., the rate of reaction is nil.; above 300°C., methane formation preponderates. If strong bases are present in the catalyst, the formation of solid paraffins is favored. The gases must be free from sulfur compounds, for these are effective catalyst poisons.[3]

When carbon monoxide is reduced at around 300°C. and with pressures in the range of 10 to 30 atmos. using iron-type catalysts, the liquid hydrocarbons are different and are more unsaturated than those obtained using cobalt-type catalysts at lower temperatures. When ruthenium is used as the catalyst and the interaction of carbon monoxide and hydrogen is carried out under 100 atmos. pressure and at about 200°C., the product is likely to be mainly solid paraffinic-type hydrocarbons with molecular weights extending to 9,000.[4]

In recent years, there has been a large amount of work done on the reduction of carbon monoxide to make liquid fuels, for this synthesis is of considerable practical value.[5]

Methanol results from the high-pressure hydrogenation of carbon monoxides at temperatures from 275 to 375°C. with catalysts composed principally of copper, zinc, chromium, manganese, and aluminum oxides.[1,2] Pressure is needed because the amount of methanol in equilibrium with carbon monoxide and hydrogen at temperatures of approximately 300°C. and at atmospheric pressure is negligible. Because of the decrease in volume attending this reaction, increase in pressure increases the yield. In this respect, the synthesis of methanol is analogous to that of ammonia from nitrogen and hydrogen. The pressures used are of the order of 3,000 lb. per sq. in. Here is a striking case of the selectivity, or preferential character, of catalysts. These methanol catalysts readily reduce carbon monoxide to methanol with only a trace of methane, even though the temperature is 375°C. and pressures are as high as 4,000 lb. per sq. in. On the other hand, carbon monoxide in contact with an active nickel catalyst results in a violent reduction to methane at temperatures of 200°C. and atmospheric pressure. The methanol-type catalysts, for some reason, are incapable of carrying the reduction to completion, *viz.*, to methane. Consequently, they are finding extensive application where mild hydrogenation conditions are needed.

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[1] Elvins and Nash, *Nature*, **118**, 154 (1926); *J. Soc. Chem. Ind.*, **45**, 878 (1926).

[2] Erdeley and Nash, *J. Soc. Chem. Ind.*, **47**, 219T (1928).

[3] Fischer, *Brennstoff-Chem.*, **8**, 1 (1927).

[4] Lowry, "Chemistry of Coal Utilization," Vol. II, pp. 1818–1840, John Wiley & Sons, Inc., New York, 1945.

[5] Storch, "Synthesis of Hydrocarbons from Water Gas," Chap. XXXIX in Lowry, *op. cit.*, Vol. II, pp. 1797–1845; Fischer and Pichler, Ber., **72B**, 327–330 (1939); *Brennstoff-Chem.*, **20**, 41–48 (1939); Fischer, *Oel u. Kohle*, **39**, 517–522 (1943); Fischer, Roelen, and Feist, *Petroleum Refiner*, **22**, 429–436 (1943); Fischer, *Petroleum Refiner*, **23**, 70–76 (1944); Komarewsky and Riesz, *Petroleum Refiner*, **23**, 415 (1944); Komarewsky, *Petroleum Refiner*, **24**, 170 (1945); Koch and Ibing, *Petroleum Refiner*, **22**, 279–286 (1943).

Higher alcohols with normal boiling points up to nearly 200°C. are formed by high-pressure hydrogenation of carbon monoxide at temperatures just above those generally used in the synthesis of methanol, *viz.*, at about 350 to 450°C. The catalysts consist of iron promoted with alkalies or methanol-type catalysts containing alkalies.[3] The mechanism of formation of these higher alcohols appears to be a series of successive condensations brought about through dehydration between smaller alcohols.[4]

$$2CH_3OH \rightarrow C_2H_5OH + H_2O$$
$$CH_3OH + C_2H_5OH \rightarrow C_3H_7OH + H_2O$$
$$2C_2H_5OH \rightarrow C_4H_9OH + H_2O, \text{ etc.}$$

Formaldehyde, acetaldehyde as well as propionic, butyric, and valeric

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[1] Frolich, Fenske, and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928); Fenske and Frolich, *Ind. Eng. Chem.*, **21**, 1052 (1929); Lazier and Vaughen, *J. Am. Chem. Soc.*, **54**, 3084 (1932); Lewis and Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928); Frolich, Fenske, Taylor, and Southwick, *Ind. Eng. Chem.*, **20**, 1327 (1928); Cryder and Frolich, *Ind. Eng. Chem.*, **21**, 867 (1929); Audibert and Raineau, *Ind. Eng. Chem.*, **20**, 1105 (1928); Huffman and Dodge, *Ind. Eng. Chem.*, **21**, 1056 (1929); Brown and Galloway, *Ind. Eng. Chem.*, **20**, 960 (1928); Smith and Branting, *J. Am. Chem. Soc.*, **51**, 129 (1929); Newitt, Byrne, and Strong, *Proc. Roy. Soc.*, **123A**, 236 (1929).

[2] Hirst, "Methanol Synthesis from Water Gas," Chap. XL in Lowry, *op. cit.*, Vol. II, pp. 1846–1868.

[3] Frolich and Lewis, *Ind. Eng. Chem.*, **20**, 304 (1928); Fischer, "The Conversion of Coal into Oils," 1st ed., trans. by Lessing, p. 213, Ernest Benn, Ltd., London, 1925; Graves, *Ind. Eng. Chem.*, **23**, 1381 (1931).

[4] Frolich and Cryder, *Ind. Eng. Chem.*, **22**, 1057 (1930); Parks and Huffman, "Free Energies of Some Organic Compounds," 1st ed., p. 224, Reinhold Publishing Corporation, New York, 1932.

aldehydes are reduced to the corresponding alcohols at about 100 to 150°C. in the presence of a nickel catalyst. However, there are side reactions, methane and water being formed.[1] The acetaldehyde, ethyl alcohol, and hydrogen equilibrium has been studied.[2]

TABLE VII.—REDUCTION OF ALDEHYDES TO ALCOHOLS

Compound	Catalyst	Temperature, °C.	Pressure, atmos.	Phase	Products obtained	Reference
Acetaldehyde	Nickel	25	110	Liquid	Ethyl alcohol	1
Heptaldehyde	Platinum oxide	25	2 to 3	Liquid	Heptyl alcohol	2
Heptaldehyde	Colloidal platinum	25 to 50	1	Dilute acetic acid solution	Heptyl alcohol	3
Furfural	Platinum oxide	20 to 60	1 to 3	Liquid	Furfuryl alcohol, tetrahydrofurfuryl alcohol, pentanediol-1, 5, pentanediol-1, 2, and *n*-amyl alcohol	4, 5
Furfural	Copper chromite	150	100 to 150	Liquid	Furfuryl alcohol	6
Benzaldehyde	Platinum black or colloidal palladium	25 to 50	1 to 3	Liquid	Benzyl alcohol, toluene, and methylcyclohexane	7, 8, 9
Benzaldehyde	Nickel	25	110	Liquid	Benzyl alcohol	1
Benzaldehyde	Copper chromite	180	100 to 150	Liquid	Benzyl alcohol	6
β-Naphthaldehyde	Platinum with ferric chloride promoter	25	2 to 3	Dilute ethanol solution	β-Naphthyl carbinol	10
Aldol	Nickel on kieselguhr	125	140 to 210	Liquid	Butanediol-1, 3	11

[1] COVERT and ADKINS, *J. Am. Chem. Soc.*, **54,** 4117 (1932).
[2] CAROTHERS and ADAMS, *J. Am. Chem. Soc.*, **46,** 1682 (1924).
[3] SKITA and MEYER, *Ber.*, **45,** 3589 (1912).
[4] PIERCE and PARKS, *J. Am. Chem. Soc.*, **51,** 3385 (1929).
[5] KAUFMANN with ADAMS, *J. Am. Chem. Soc.*, **45,** 3029 (1923).
[6] ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53,** 1093 (1931); U.S. 2,094,975 (1937).
[7] CAROTHERS and ADAMS, *J. Am. Chem. Soc.*, **45,** 1071 (1923).
[8] SKITA, *Ber.*, **48,** 1486 (1915).
[9] VAVON, *Compt. rend.*, **154,** 359 (1912).
[10] CAMPBELL, ANDERSON, and GILMORE, *J. Chem. Soc.*, **1940,** 819–821.
[11] ADKINS and CONNOR, *J. Am. Chem. Soc.*, **54,** 4678 (1932).

A new synthesis of higher alcohols has been developed in Germany known as the "OXO" synthesis.[3] Aliphatic olefins are reacted in the liquid phase under pressure with carbon monoxide and hydrogen with the use of catalysts to produce the corresponding aldehydes. These are subsequently hydrogenated to the primary alcohols.

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[1] SABATIER and SENDERENS, *Compt. rend.*, **137,** 302 (1903).

[2] BANCROFT, and GEORGE, *J. Phys. Chem.*, **35,** 2194 (1931).

[3] NATTA, *Chimica e industria (Italy)*, **24,** 389–393 (1942); *C.A.*, **38,** 4252 (1944).

The reduction of ketones by hydrogen at elevated temperatures is also a reversible reaction. Thus, in the case of acetone, at 218°C. and

TABLE VIII.—REDUCTION OF KETONES TO ALCOHOLS

Compound	Catalyst	Temp., °C.	Pressure, atmos.	Phase	Products obtained	Reference
Acetone..........	Nickel	115 to 125	1	Vapor	Isopropyl alcohol	1
Acetone..........	Platinum black	25	1 to 2	Acetic acid solution	Isopropyl alcohol	2
Acetone..........	Nickel	23	2 to 3	Liquid	Isopropyl alcohol	3
Acetone..........	Copper chromite	150	100 to 150	Liquid	Isopropyl alcohol	4
Methyl ethyl ketone	Platinum oxide	25 to 50	1 to 3	Liquid	Secondary butyl alcohol	5
Diethyl ketone...	Nickel	130 to 140	1	Vapor	Diethylcarbinol	1
Diethyl ketone...	Colloidal platinum	25	1 to 3	Acetic acid solution	Diethylcarbinol	6
Diethyl ketone...	Platinum black	25	1 to 2	Acetic acid solution	Diethylcarbinol	2
Methyl isopropyl ketone	Copper chromite	150	100 to 150	Liquid	Methylisopropylcarbinol	4
Methyl butyl ketone	Nickel	150	1	Vapor	Methylbutylcarbinol	1
Methyl isobutyl ketone	Nickel	150	120	Liquid	Methylisobutylcarbinol	7
Methyl isobutyl ketone	Platinum or palladium black	25	1 to 2	Liquid	Methylisobutylcarbinol	2
Pinacoline........	Copper chromite	150	100 to 150	Liquid	Methyl-*tert*-butylcarbinol	4
Acetylacetone....	Nickel	140 to 160	1	Vapor	Pentanediol-2, 4 and pentanol-2	8
Acetylacetone....	Colloidal platinum	25 to 50	1 to 3	Acetic acid solution	Methylpropylcarbinol	6
Acetylacetone....	Platinum black	25	1 to 2	Ether or alcohol solution	Methylpropylcarbinol	2
Acetophenone....	Platinum black	25	1 to 2	Alcohol-water solution	Methylphenylcarbinol	2
Acetophenone....	Platinum black	25	1 to 2	Acetic acid solution	Ethylcyclohexane	2
Acetophenone....	Nickel	175	120	Liquid	Methylphenylcarbinol and ethylcyclohexane	7
Benzophenone....	Platinum black	25	1 to 2	Ether solution	Diphenylcarbinol	2
Quinone.........	Nickel	200	1	Vapor	Hydroquinone	9

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[1] Sabatier and Senderens, *Compt. rend.*, **137**, 302 (1900).

[2] Vavon, *Ann. chim.*, **9**, 1, 144 (1914).

[3] Covert and Adkins, *J. Am. Chem. Soc.*, **54**, 4117 (1932).

[4] Adkins and Connor, *J. Am. Chem. Soc.*, **53**, 1093 (1931).

[5] Voorhees with Adams, *J. Am. Chem. Soc.*, **44**, 1404 (1922).

[6] Skita, *Ber.*, **48**, 1496 (1915).

[7] Covert, Connor, and Adkins, *J. Am Chem. Soc.*, **54**, 1658, 1932.

[8] Sabatier and Mailhe, *Compt. rend.*, **144**, 1086 (1907).

[9] Sabatier and Mailhe, *op. cit.*, **146**, 457 (1908).

atmospheric pressure, the hydrogenation is about only 30 per cent complete.[1] However, this is not a serious factor, for the hydrogenation is accompanied by a decrease in volume so that increased hydrogen pressure counteracts the effect of increased temperature on the equilibrium yield. In order to give conveniently the various conditions under which aldehydes or ketones may be hydrogenated, a few typical examples are summarized in Tables VII and VIII.

Hydrogenation of Esters and Acids.

General Reaction.

$$R{\cdot}COOR' + 2H_2 \rightarrow RCH_2OH + R'OH,$$

where R is usually an aliphatic group, and R′ is the same or a hydrogen atom. The carboxyl group in esters and acids can be reduced to the corresponding hydroxyl group by the use of mild hydrogenating catalysts and hydrogen pressures, generally of the order of 100 atmos. or more. It is necessary that the hydrogenation conditions be controlled carefully in order to avoid dehydration of the alcohol—resulting in an olefin—or if the latter is further reduced by hydrogen, a paraffin hydrocarbon is formed. In general, the catalysts are of the type used in synthesizing methanol and higher alcohols. The reduction of the carboxyl group is most satisfactory in aliphatic or hydroaromatic compounds. In the aromatic series, the reduction to alcohols also occurs, the best results being obtained when the carboxyl group is in an aliphatic chain. If the group is directly attached or near to an aromatic ring, side reactions usually accompany the reduction. These generally involve the reduction of the alcohol group to a hydrocarbon group. Typical reductions are summarized in Table IX.

Hydrogenolyses Involving Cleavages of Carbon-to-oxygen and Carbon-to-carbon Bonds.—Hydrogenolysis is a more exact expression than destructive hydrogenation and refers particularly to cleavages in a molecule associated with the addition of hydrogen to the molecule. The cleavages discussed here are of carbon-to-carbon and carbon-to-oxygen bonds. There may also take place the breaking of carbon-to-nitrogen, -sulfur, or -halogen bonds, as occurs in hydrogenations in which these elements are usually eliminated as ammonia, hydrogen sulfide, or hydrogen halides. Hydrogenolysis is a term analogous to hydrolysis, alcoholysis, or ammonolysis in which a double decomposition is accomplished by means of water, alcohol, or ammonia, respectively.

Thus:

$$C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O \rightarrow 2C_2H_5OH \text{ (hydrolysis)}$$
$$C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2 \rightarrow C_2H_6 + C_2H_5OH \text{ (hydrogenolysis)}$$

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[1] Parks and Huffman, "Free Energies of Some Organic Compounds," p. 23, Reinhold Publishing Corporation, New York, 1932.

TABLE IX.—REDUCTION OF ESTERS AND ACIDS TO ALCOHOLS, ETC.

Compound	Catalyst	Temperature, °C.	Pressure, atmos.	Phase	Products obtained	Reference
Methyl formate	Copper	180 to 230	1	Vapor	Methanol	1
Acetic acid	Zinc-manganese chromium oxide	400	200	Vapor	Ethyl, propyl, and butyl alcohols	2
Acetic acid	Copper-zinc cadmium chromite	390	170 to 200	Vapor	Ethyl alcohol and ethyl acetate	3
Ethyl lactate	Copper chromite	250	200 to 300	Vapor-liquid	Propanediol-1, 2	4
Butyric acid	Copper-zinc cadmium chromite	390	150 to 200	Vapor	Butyl alcohol and butyl butyrate	3
Ethyl succinate	Copper chromite	250	220	Liquid	Tetramethylene glycol	5
Ethyl trimethylacetate	Copper chromite	250	220	Liquid	Tertiary butylcarbinol	5
Ethyl valerate	Copper chromite	250	220	Liquid	*n*-Amyl alcohol	5
Di-*n*-butyl glutarate	Copper chromite	250	200 to 300	Liquid	Pentanediol-1, 5	
Methyl, ethyl or butyl caproate	Copper chromite	250	200 to 300	Liquid	*n*-Hexyl alcohol	4
Caprylic acid	Copper on kieselguhr	340	200	Liquid	*n*-Octyl alcohol	6
Methyl caprate	Copper on kieselguhr	300 to 325	250 to 285	Liquid	*n*-Decyl alcohol	6
Diethyl sebacate	Copper chromite	250	200 to 300	Liquid	Decanediol-1, 10	4
Sebacic acid	Copper chromite	390 to 400	200	Ethyl alcohol solution	Decanediol-1, 10	3
Coconut oil acids	Copper-zinc cadmium chromite	380	200	Liquid	*n*-Decyl alcohol, lauryl alcohol, and higher molecular weight alcohols	3
Lauric acid	Copper-zinc cadmium chromite	380	200	Liquid	Lauryl alcohol, and lauryl laurate	3
Methyl laurate	Zinc-copper chromite	300 to 325	270 to 290	Liquid	Lauryl alcohol	5–6
Oleic acid	Copper-zinc cadmium chromite	350 to 420	200	Liquid	Oleyl alcohol, stearyl alcohol and esters	3
Stearic acid	Zinc-copper chromite	325	280	Liquid	Stearyl alcohol	6
Ethyl cinnamate	Copper chromite	250	200	Liquid	3-Phenylpropanol-1	5
Methyl salicylate	Copper chromite	250	200 to 300	Liquid	2-Methylcyclohexanol and o-cresol	4
Ethyl hexahydrobenzoate	Copper chromite	250	200 to 300	Liquid	Cyclohexylcarbinol	4
Ethyl α-phenylbutyrate	Copper chromite	250	200 to 300	Liquid	2-Phenylbutanol-1 and hydrocarbons	4
Ethyl β-phenylpropionate	Copper chromite	250	200 to 300	Liquid	3-Phenylpropanol-1	4
Ethyl phenylacetate	Copper chromite	250	200 to 300	Liquid	2-Phenylethanol-1 and ethylbenzene	4

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[1] CHRISTIANSEN, *J. Chem. Soc.*, **1926**, 413.

[2] FROLICH and CRYDER, *Ind. Eng. Chem.*, **22**, 1057 (1930): CRYDER, Doctor's thesis, Chem. Eng., Mass. Inst. Tech., 1930.

[3] Lazier, U. S. 1,839,974 (1923).

[4] FOLKERS and ADKINS, *J. Am. Chem. Soc.*, **54**, 1146 (1932).

[5] ADKINS and FOLKERS, *J. Am. Chem. Soc.*, **53**, 1096 (1931).

[6] SCHRAUTH, SCHENK, and STICKDORN, *Ber.*, **64B**, 1314 (1931).

In practically all hydrogenations, undesirable side reactions occur, although in some instances only to a negligible extent. These side reactions are usually cases of hydrogenolysis. This type of hydrogenation has been emphasized and studied by Ellis and Adkins.[1,2] It has certain applications to problems of petroleum refining and to synthetic organic chemistry. In the hydrogenation of petroleum, coals, and tars, the application pertains to the elimination of sulfur, nitrogen, or oxygen and to the conversion of heavy, tarry, or asphaltic substances to more desirable hydrocarbon products usually of a more paraffinic or saturated type. The synthetic applications are concerned with the preparation of new compounds or with a simplified and more economical production of known compounds, either from the usual and known types of raw materials or from new or relatively undeveloped ones.

The following tables (X to XII) illustrate the type of hydrogenolysis involving the breaking of carbon-to-carbon and carbon-to-oxygen bonds. In general, hydrogenolysis is favored by increased temperature, higher hydrogen pressures, and the more violent type of hydrogenating catalysts. However, these conditions may prove so violent that a variety of reaction products results. From a synthesis viewpoint, the cleavage of the different bonds is best controlled by a careful choice of the reaction temperature, the time of contact, the hydrogen pressure, and the type of catalyst. Frequently, in cases of carbon-to-oxygen cleavage, it may be desirable to incorporate a dehydrating catalyst along with the hydrogenating catalyst. Catalysts such as nickel-alumina and nickel-thoria are of this type. Finally, the point and the type of cleavage (whether carbon-to-carbon or carbon-to-oxygen) are profoundly influenced by the position of various substituent groups, the branching of the carbon chain, and the type of group, *viz.*, aliphatic or aromatic, near or adjacent to the point of cleavage.

Phenols and cresols can be reduced to the corresponding hydroaromatic or aromatic hydrocarbons, depending on the temperature, the pressure of hydrogen, and the type of catalyst. These reactions are increasing in technical importance, for they are the type occuring in the hydrogenation of undesirable phenolic tars to valuable petroleum products. Phenol ($C_6H_5{\cdot}OH$), at temperatures above 250°C. and with a nickel catalyst, is reduced by hydrogen to benzene; and polyphenols, *e.g.*, di- and trihydroxybenzenes, are reduced even more readily to benzene.[3] With hydrogen at pressures of 1,250 lb. per sq. in. and in the

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[1] ELLIS, "Hydrogenation of Organic Substances," 3d ed., p. 564, D. Van Nostrand Company, Inc., New York, 1930.

[2] ADKINS, "Reactions of Hydrogen," p. 69, The University of Wisconsin Press, Madison, Wis., 1937.

[3] MAILHE and GODON, *Bull. soc. chim.* [4] **21,** 61 (1917); SABATIER and MAILHE,

TABLE X.—HYDROGENOLYSIS OF OXYGENATED COMPOUNDS

Compound	Catalyst	Temperature, °C.	Pressure, atmos.	Phase	Products obtained	Reference
Ethyl ether	Nickel	250	1	Vapor	Ethane and ethyl alcohol	1
Acetone	Nickel	300	100	Vapor	Propane	2
Methylhexylcarbinol	Nickel	300	100	Vapor	*n*-Hexane and *n*-octane	3
Benzyl alcohol	Nickel	375	1	Vapor	Toluene	4
Benzyl ethyl ether	Nickel	175	120	Liquid	Toluene and ethyl alcohol	5
Benzaldehyde	Nickel	230	1	Vapor	Toluene and benzene	6
Acetophenone	Nickel	250	1	Vapor	Ethylbenzene, and ethylcyclohexane	7
Benzophenone	Nickel	300	1	Vapor	Diphenylmethane	8
Benzophenone	Copper chromite	175	100 to 150	Liquid	Diphenylmethane	9
Phenyl ethyl ketone	Nickel and copper	300	1	Vapor	Propylbenzene	8
Benzoylacetone	Nickel	200	1	Vapor	Butylbenzene	10
Propanediol-1, 3	Copper chromite	250	175	Liquid	*n*-Propyl alcohol	11
Butanediol-1, 3	Copper chromite	250	175	Liquid	Butanol-2 and *n*-butyl alcohol	11
2-Methylpentanediol-2, 4	Copper chromite	200	175	Liquid	Isopropyl alcohol and 2-methylpentanol-4	11
Pinacolone	Molybdenum sulfide	350	80	Xylene solution	2, 3-Dimethylbutane	12

[1] ELLIS, "Hydrogenation of Organic Compounds," 3d ed., p. 564, D. Van Nostrand Company, Inc., New York, 1930.

[2] IPATIEV, *Ber.*, **20,** 1281 (1907).

[3] HERSH and GRAHAM, Undergraduate thesis, Penn. State Coll. (1931).

[4] SABATIER and SENDERENS, *Bull. soc. chim.*, **33,** 616 (1905).

[5] COVERT, CONNOR, and ADKINS, *J. Chem. Soc.*, **54,** 1658 (1932).

[6] SABATIER and SENDERENS, *Compt. rend.*, **137,** 302 (1903).

[7] GRIGNARD, *Bull. soc. chim.*, **43,** 473 (1928).

[8] SABATIER and MURAT, *Ann. chim.* [9] **4,** 257 (1915).

[9] ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53,** 1093 (1931).

[10] DARZENS, *Compt. rend.*, **139,** 868 (1904).

[11] CONNOR and ADKINS, *J. Am. Chem. Soc.*, **54,** 4678 (1932).

[12] MOLDAVSKÜ and NIZOVKINA, *J. Gen. Chem. (U.S.S.R.)*, **10,** 653 (1940); *C.A.* **34,** 7843 (1940).

absence of catalysts, phenol is unchanged after heating for 2½ hr. at 460 to 470°C. Under the same conditions but with alumina as a catalyst, a 45 per cent yield of benzene is obtained in 4 hr. Additional data on the hydrogenolysis of phenol to benzene hydrocarbons at high pressure are given in Table XI.[1]

Cresols and other hydrocarbons, when passed along with hydrogen through tubes at temperatures of about 750°C., yield aromatic hydro-

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Compt. rend., **145,** 1126 (1907); SABATIER and SENDERENS, *Ann. chim. phys.* [8], **4,** 429 (1905).

[1] KLING and FLORENTIN, *Intern. Conf. Bituminous Coal*, II, 33 (1931).

carbons;[1] the best results were obtained with a tinned tube, whereas with porcelain tubes, the yields were negligible. Table XII summarizes the results.

Technical *m*-cresol at 720 to 730°C., with from 3½ to 8 times the theotheoretical amount of hydrogen, gives 95 to 98 per cent of the theoretical yield of benzene. With smaller amounts of hydrogen, the yields are less.[2]

TABLE XI.—HYDROGENOLYSIS OF PHENOL

Catalyst	Pressure, lb. per sq. in.		Max. temp., °C.	Total time, min.	Total liquid yield	Fraction below 120°C.		Yield of benzene hydrocarbons[1]
	Initial	Max.				%	Density, 15°C.	
W_2O_5	1,400	4,600	485	240	90	44	. . . .	39.6
Mo_2O_5	1,400	3,100	500	240	80	43	0.868	34.4
Mo_2O_5	1,400	3,500	500	90	92	43	0.849	39.5
Mo_2O_5	1,600	4,200	490	100	80	90	0.806	72
MoO_3 (activated)	1,600	4,500	488	100	82	61	0.822	50[2]
MoO_3 (activated)	1,600	4,200	488	90	76	84	0.818	64
Al_2O_3	1,200	3,700	485	300	45	82	0.868	37
Al_2O_3 (activated)	1,200	4,700	490	240	80.5	66.5	0.863	54.5
Al_2O_3 + 20 % Mo_2O_5 (activated)	1,200	4,300	490	240	75	87.5	0.840	65.5
Al_2O_3 + Cr_2O_3 + Mo_2O_5 (activated)	1,200	3,400	488	90	75.6	85	0.845	64.3
ThO_2 + Mo_2O_5 (activated)	1,200	4,200	478	150	69.5	87	0.838	60.5
NiO + Al_2O_3 (activated)	1,200	2,700	475	120	74	62.5	0.775	46.4
MoS_2	1,200	4,100	480	100	71.6	82	0.821	59.5
NiO + Al_2O_3 (activated)	1,850	4,100	472	90	80	70	0.792	56
Cyclohexanol alone	1,400	4,600	475	90[3]	100[4]			

[1] Does not include losses and light hydrocarbons entrained by the gases.

[2] Theoretical amount of hydrogen to change phenol to cyclohexane.

[3] Thirty minutes at 75°C.

[4] The resultant liquid boiled 50 to 90°C.; density, 0.760 (15°C.).

The marked influence of structure on the type of cleavage occuring during hydrogenolysis of hydroxybenzenes is illustrated by the following two examples. Thus, cyclohexanediol-1, 3 [$C_6H_{10}{\cdot}(OH)_2$] at about 250°C., with a copper chromite catalyst and 175 atmos. hydrogen pressure, gives a 95 per cent yield of cyclohexanol ($C_6H_{11}{\cdot}OH$). The 1, 2-isomer is more difficult to reduce; under the same conditions, only about 20 per cent of cyclohexanol forms. The 1, 4-isomer undergoes hydrogenolysis to only a very slight extent, 96 per cent of the material being recovered unchanged after heating for over 8 hr. under the same conditions as for the 1, 3- or 1, 2-isomers.[3] The second example pertains to the xylenols ($(CH_3)_2 \cdot C_6H_3 \cdot OH$), which with nickel and hydrogen at about 200°C. exhibit varying degrees of hydrogenolysis, depending on the position of the methyl and the hydroxyl groups. Thus 1, 3, 4-xylenol and 1, 4, 2-xylenol give relatively high yields of the corresponding dimethylcyclohexanols, whereas 1, 2, 4-xylenol, under substantially the same conditions, gives ortho xylene as the principal product.[1]

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[1] MORRELL and EGLOFF, *Intern. Conf. Bituminous Coal.* II, 587 (1928).

[2] FISCHER and SCHRADER, *Ges. Abhandl. Kenntnis Kohle*, **6**, 128–144 (1921).

[3] CONNOR and ADKINS, *J. Am. Chem. Soc.*, **54**, 4678 (1932).

Table XII.—Hydrogenolysis of Phenols and Hydrocarbons at 750°C.

Material	Yield as aromatic hydrocarbons, %	
	Tinned tube	Iron tube
Three mixed cresols	64	5
o-Cresol	72	35
1, 3, 4-Xylenol	72	5
Hexane	7	4
Solvent naphtha I	61	63
Solvent naphtha II	49	48

Hydrocarbons, depending on the length of the chain or branching in the chain or the ring structure, under the combined action of hydrogen, catalysts, and heat, undergo certain cleavages that involve the splitting off of groups or molecular fragments or the opening of ring structures, The resulting products are then usually smaller molecules, are of a more stable type, and usually contain a higher percentage of hydrogen than the original material. The opening of the ring may first involve the reduction to a hydroaromatic of naphthene structure, followed by the opening of the ring with the formation of a chain or paraffin structure. These reactions are also of great technical importance, for they are probably the type of reaction occuring in the hydrogenation of heavy petroleum residues or asphaltic or aromatic base oils, whereby conversion takes place in high yields to stable, more volatile petroleum products such as gasoline and kerosene.

The hydrogenation and hydrogenolysis of carbohydrates has been the subject of considerable research in recent years. Glucose, sucrose, molasses, starch, and other saccharides have been treated with hydrogen at temperatures ranging from 100 to 250°C. and pressures from 80 to 300 atmos., using nickel, iron, and copper catalysts, to prepare propylene glycol and glycerol in good yields.[2] Lesser quantities of hexyl alcohol, ethylene glycol, ethanol, and methanol are also formed. By a two-stage hydrogenation of hexose some 1,530 tons of glycerogen (a glycerin substitute) containing 40 per cent glycerol, 40 per cent propylene glycol, and 20 per cent hexyl alcohol were produced in Germany during the war.[1]

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[1] Sabatier and Mailhe, *Compt. rend.*, **142**, 553 (1906).

[2] Natta, Rigamonti, and Beati, *Ber.*, **76B**, 641–656 (1943); Stengel, U. S. 2,325,206 (1943); *C.A.*, **38**, 375 (1944); Yosikawa and Hanai, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **17**, 1262–1277 (1938); *C.A.*, **34**, 2796 (1940).

Acetoacetic ester derivatives, which play an important part in various syntheses, offer interesting examples of different types of hydrogenolysis.[2]

IV. PHYSICAL FACTORS OTHER THAN CATALYSTS AFFECTING HYDROGENATION

The Reaction Must Be Possible.[3]—Since catalysts affect only the rate or speed of a reaction and have nothing to do with the inherent tendency of a reaction to proceed, it is obviously of real importance to know whether or not the reaction is at all possible for the conditions of temperature and pressure chosen. The concern is then with chemical affinity; and since the free-energy change of a definite, specific reaction is a quantitative measure of such chemical forces, it is desirable to have free-energy data on the substances in question if such data can be had. If reliable free-energy data show the reaction to be possible, then experimental work may be started in order to find suitable catalysts that will enable the reaction to proceed at a reasonable rate.

It is difficult to get accurate free-energy data on a large number of organic compounds, but a reasonable amount of fairly reliable data are now available.[4] Figures 1*A*, 1*B*, 1*C*, 1*D*, 1*E*, 1*F*, 1*G*, and 1*H* give free-energy values for a few compounds of industrial importance. The values are for the free energy of formation from the elements of the substance in question in the gaseous state at 1 atmos. pressure. Values are given for two temperatures: 100 and 400°C. It is permissible to make linear interpolation between these temperatures; *i.e.*, a value at 250°C. will lie midway between the 100 and 400°C. values. To point out the relationships that exist in these straight-chain aliphatic compounds, the free-energy content per carbon atom is plotted. Therefore, to get the molal value, these values (ordinates) must be multiplied by the number of carbon atoms in the straight-chain aliphatic compound in question. Figures 1*A*, 1*B*, and 1*C* give, respectively, the free-energy values for carbon monoxide, water, and carbon dioxide, all in the gaseous state at 1 atmos. pressure. Figures 1*D* and 1*E* give free-energy values for the straight-chain olefins and paraffins.

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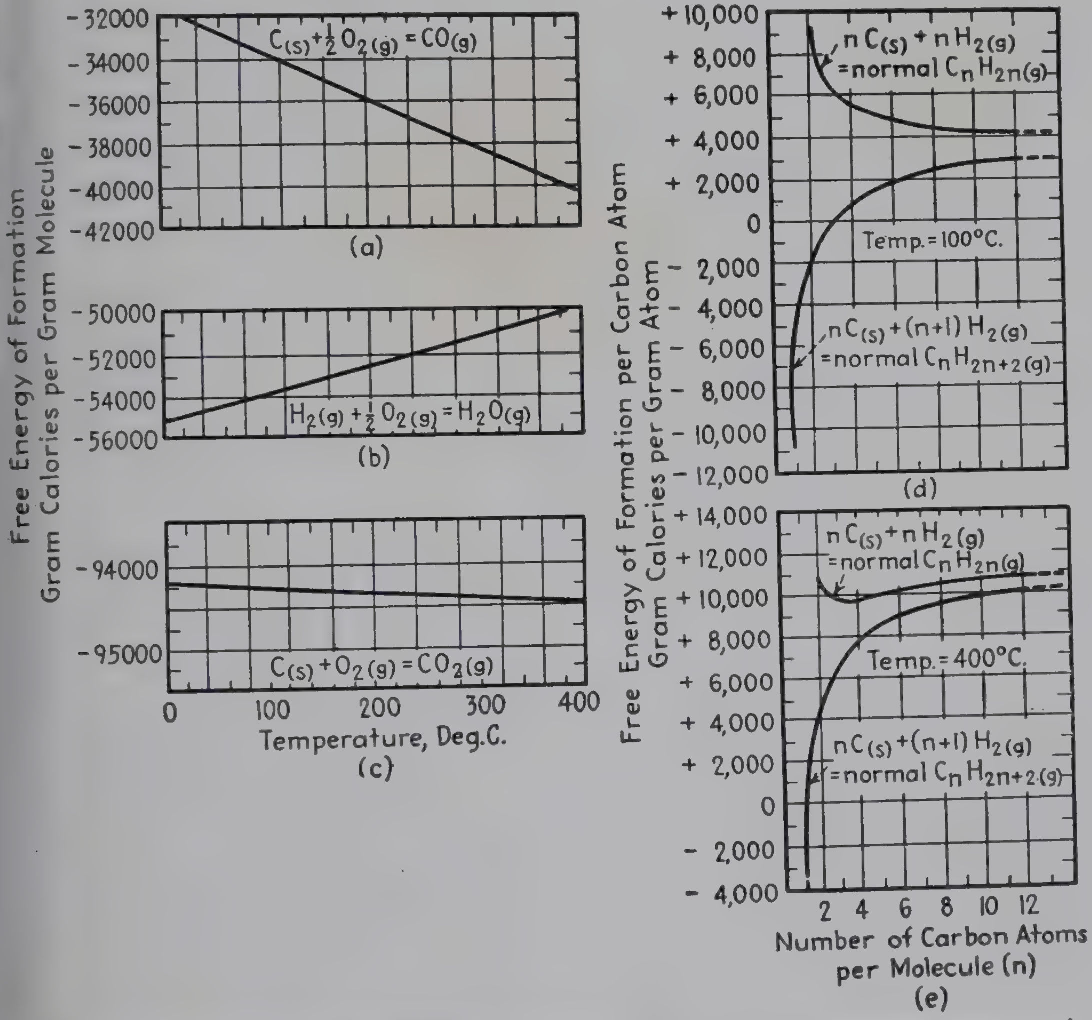
[1] *Declassified Rep't. 183*, office of the Publication Board. Reported by Leaper.

[2] Connor and Adkins, *J. Am. Chem. Soc.*, **54**, 4678 (1932).

[3] Examples of the use of free-energy data may be extended into a long list. Such is not the intention of this discussion. Applications have been made to only the four types of reduction that this chapter is concerned with, *viz.*, ethylenic, carbonyl, and carboxyl linkages and hydrogenolysis or destructive hydrogenation. The purpose has been to show the method of applying free-energy data to such reductions and the nature of the results and conclusions that are possible therefrom. It should be pointed out that free-energy data on organic compounds are a comparatively recent development in the field of organic chemistry. Consequently, the data given here may in many cases be found to be wanting in accuracy. Nevertheless, rather than to ignore their usefulness and possibilities, it is believed to be better to show that at least semiquantitative conclusions may be drawn from them that would not otherwise be possible. On this basis alone, their use is justified.

[4] Parks and Huffman, "Free Energies of Some Organic Compounds," Reinhold Publishing Corporation, New York, 1932.



Figs. 1*A*, *B*, *C*, *D*, *E*.—Free energy of formation of CO, H_2O, CO_2, normal olefins, and normal paraffins in the gaseous state.

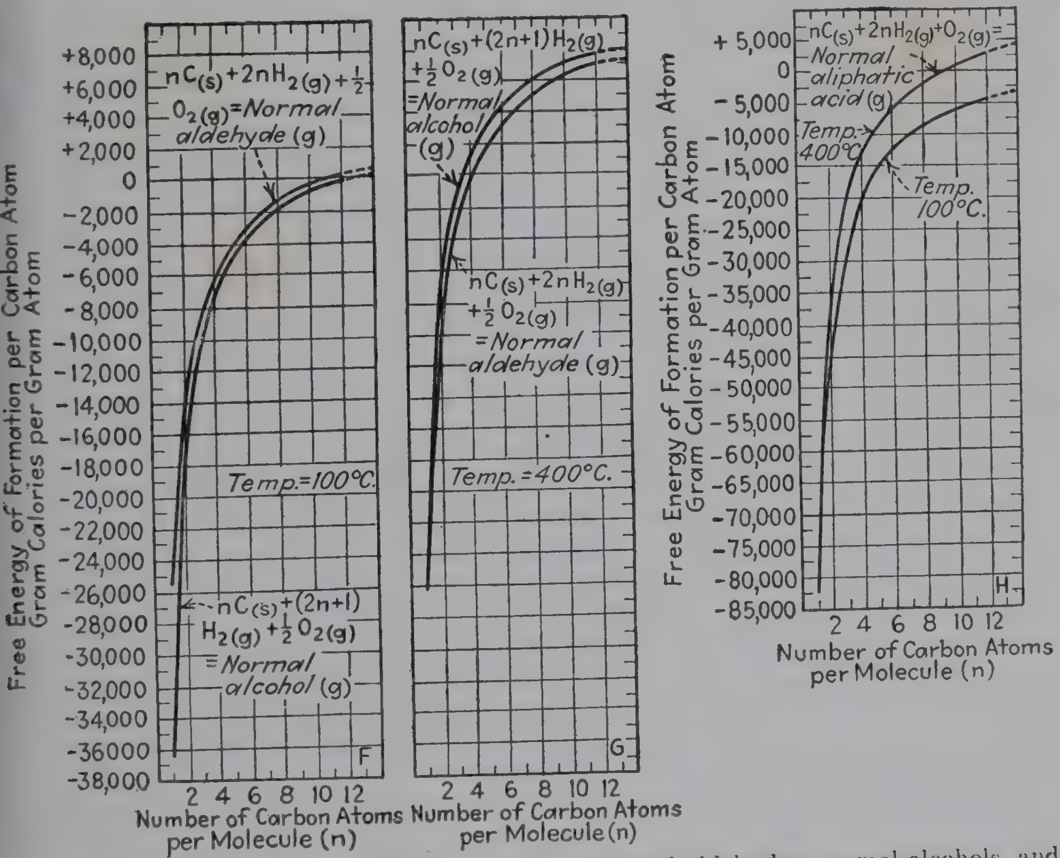
When all the reactants and products are in the gaseous state at a partial pressure of 1 atmos., then the well-known relationship exists:

$$-\Delta F = 4.57T \log K \tag{1}$$

The term $-\Delta F$ is the free-energy decrease in calories for the reaction as it proceeds from left to right. It represents the difference in free-energy content of all the reactants and all the products. On the basis used here for free-energy values, all elements in their normal state of aggregation at 1 atmos. pressure, and at any particular temperature T are arbitrarily assigned the value of zero free energy. In this way, the free-energy content of all compounds will have plus or minus values, since the free-energy content at any temperature T is merely the free energy of formation from the elements at T. In Eq. (1), T is the absolute temperature in degrees Kelvin, and K is the equilibrium constant for the reaction, with the products appearing in the numerator and the reactants in the denominator in terms of the individual partial pressures expressed in the unit of atmospheres. In making calculations, this system of units must be definitely adhered to in using Eq. (1). From the equilibrium constant of a chemical reaction, it is of course possible to calculate in the usual way the ultimate yields that may be expected and also to determine quantitatively the effect of pressure on the equilibrium conversion for those reactions affected by pressure, *viz.*, those attended by a change in the number of gaseous moles. And if the equilibrium conversion at another temperature is wanted, then the free-energy change at that temperature only need be evaluated.

All spontaneous reactions, *i.e.*, those proceeding of their own accord and in the absence of any electrical influences, such as magnetic or electrostatic forces, or various forms of radiation, are attended by a free-energy decrease. If a reaction involves only one compound and an element, *e.g.*, hydrogen, yielding as the product only one other compound of the same number of carbon atoms, then the compound with the lower free energy is the more stable of the two under the experimental conditions chosen. Thus, it is seen in connection with Fig. 1*D* that the normal paraffins at 100°C. have lower free-energy values than the normal olefins; *i.e.*, at this temperature, all normal olefins are capable of being hydrogenated to normal paraffins with good equilibrium yields. However, at 400°C. (Fig. 1*E*), it is seen that the free-energy difference is not so large and, for the higher olefins, the free-energy decrease on hydrogenation is very small and approaches zero. From Eq. (1), if $\Delta F = 0$, then the equilibrium constant is unity, and so it follows that the reverse reaction at this temperature is capable of proceeding to a reasonable degree. Such reactions occur in the cracking or pyrolysis of hydrocarbons, and it is well known that these pyrolytic reactions are carried out at temperatures in the vicinity of 400°C.

From Figs. 1*D* and 1*E*, it can be calculated that at 400°C. in the case of a larger paraffin, *e.g.*, hexane, there is a spontaneous tendency to decompose or crack, yielding a smaller paraffin and smaller olefin, *e.g.*, propane and propylene. At 100°C., such a reaction does not tend to occur. Therefore, if a relatively large olefin were to be hydrogenated to a paraffin of the same molecular weight, apparently it be would desirable to carry out such a reduction at lower temperatures for two pertinent reasons: (1) The equilibrium yield is better; (2) decomposition or side reactions are less likely to be troublesome. Because of this preferred lower temperature operation, catalysts must be available to operate at these lower temperatures. Such hydrogenation catalysts are known, as was pointed out earlier in this chapter (page 498).



FIGS. 1*F*, *G*, *H*.—Free energy of formation of normal aldehydes, normal alcohols, and normal aliphatic acids in the gaseous state.

Inspection of Figs. 1*F* and 1*G* shows that the reduction of aldehydes to alcohols parallels, in many respects, that of olefins to paraffins. At 100°C., it is seen that the normal alcohols have lower free-energy values than the corresponding aldehyde. Hydrogenation is, therefore, feasible if catalysts can be found to effect the reduction with reasonable speed. At higher temperatures, *e.g.*, 400°C., the aldehyde is seen to possess a lower free-energy value than the alcohol. In other words, the normal spontaneous tendency at this temperature is for the alcohols to dehydrogenate to yield aldehydes. Since the reduction goes with a volume decrease, it is possible to carry it out at this temperature by the application of pressure; but without pressure, reduction would not be feasible at 400°C. Further studies will show that as in the case of the paraffin hydrocarbons, there is the tendency at the higher temperatures to crack or decompose into lower molecular-weight hydrocarbons and that also at all temperatures, there is the decided tendency to continue the reduction to the hydrocarbon stage (hydrogenolysis). In other words, these few observations indicate that the reduction of aldehydes is apt to be beset with side reactions, and, in general, unless carefully chosen conditions are used, this is the actual fact.

The data of Fig. 1 may be applied to some of the various reductions of carbon monoxide. The simplest may be indicated by the following reaction at 400°C.:

$$\begin{aligned} CO_{(g)} + 3H_{2(g)} &= CH_{4(g)} + H_2O_{(g)} \qquad (2)\\ -40{,}500 + 0 + \Delta F &= -3{,}600 - 50{,}000\\ \Delta F &= -13{,}100 \text{ cal. at } 400°\text{C.} \end{aligned}$$

This free-energy decrease shows that at this temperature, reduction of carbon monoxide to methane is a very complete reaction as judged by the equilibrium yield that is possible. However, as indicated elsewhere, most hydrogenation reactions are reversible; if the above reaction is considered in the reverse direction, then it is seen to be the reaction indicated on page 494 for obtaining hydrogen from hydrocarbons by causing them to react with steam at temperatures of about 1000°C. where the reverse of reaction (2) is possible.

In this connection, it might be proposed to carry out a reaction as follows:

$$\begin{aligned} CH_{4(g)} + H_2O_{(g)} &= CH_3OH_{(g)} + H_{2(g)} \qquad (3)\\ -3{,}600 - 50{,}000 + \Delta F &= -26{,}000 + 0 \text{ at } 400°\text{C.}\\ \Delta F &= +27{,}400 \text{ cal. at } 400°\text{C.} \end{aligned}$$

Although it would be highly desirable to carry out such a reaction, thereby making natural gas into a more valuable product, the magnitude of this free-energy increase indicates the impossibility of so doing at any practical temperature level. It is useless, therefore, to expend any effort in this direction. The reverse reaction is obviously predominating.

Instead of the complete hydrogenation of carbon monoxide, the partial reduction to methanol might be considered.

$$\begin{aligned} CO_{(g)} + 2H_{2(g)} &= CH_3OH_{(g)} \qquad (4)\\ -34{,}000 + 0 + \Delta F &= -36{,}500 \text{ at } 100°\text{C.}\\ \Delta F &= -2{,}500 \text{ cal. at } 100°\text{C.} \end{aligned}$$

This free-energy decrease indicates that the reaction is possible at 100°C., but, so far, no catalysts have been found sufficiently active to bring about reaction at this relatively low temperature. To get increased reaction rate, it is logical to raise the temperature. If the same calculation is made by means of Figs. 1*A* and 1*G* for 400°C., the free-energy increase is found to be +14,300 cal. Thus, the above reaction is not capable of proceeding to any practical extent at this temperature even though it might be expected that now the reaction velocity might be favorable. However, the reaction as written above and the free-energy value given are for all reactants and products at 1 atmos. partial pressure. Since the reaction goes with a decrease in the number of gaseous moles, then the equilibrium yield, which is negligible at 400°C. and low pressures, can be raised to an appreciable value by working at high pressure. So it is concluded that higher reaction temperatures, *i.e.*, those up to perhaps 400°C., are allowable and so will help the reaction velocity, provided pressure is applied to increase the equilibrium yield. There then remains the problem of finding a particular unusual type of catalyst that will allow the reduction to proceed to only methanol under these rather severe conditions, for, as indicated above, there is a pronounced tendency to reduce carbon monoxide completely to methane. Certain metallic oxide catalysts have been found experimentally to possess this property (pages 504, 530), thus making the methanol synthesis from water gas a practical reality.

In the same way, and from similar reasoning from the data of Figs. 1*C* and 1*G*, it is apparent that methanol may be synthesized from a carbon dioxide-hydrogen mixture, rather than from carbon monoxide and hydrogen, should this be desired.

The Fischer-Tropsch atmospheric or low-pressure synthesis, from water gas, of hydrocarbons larger than methane may be analyzed by the data given in Fig. 1. It is found that such reactions are entirely possible even at atmospheric pressure and temperatures up to 400°C. However, it should again be realized that the higher molecular-weight hydrocarbons that result from this synthesis are likely to be further reduced to methane, since methane is the most stable hydrocarbon at temperatures below 400°C. This destructive hydrogenation or hydrogenolysis would be more apt to occur at higher temperatures, for all reaction velocities are increased, and the specificity of a catalyst is, in general, markedly reduced. Temperature control has been found to be a highly important factor in the successful operation of this process. Also, in addition to hydrogenating tendencies, it follows that the catalyst must have condensation properties to build up hydrocarbons having higher molecular weights than methane.

It is possible to analyze the mechanism indicated on page 505 for the higher alcohol synthesis. This may be typified by:

$$2\mathrm{CH_3OH}_{(g)} = \mathrm{C_2H_5OH}_{(g)} + \mathrm{H_2O}_{(g)} \tag{5}$$

$$2(-26{,}000) + \Delta F = 2(-8{,}400) - 50{,}000 \text{ at } 400°\text{C.}$$

$$\Delta F = -14{,}800 \text{ cal. at } 400°\text{C.}$$

This condensation is then entirely possible, for the reaction proceeds with a relatively large free-energy decrease. To carry out such a reaction, catalysts possessing dehydration as well as condensation properties would be desirable. Thus, free-energy data are useful not only in determining whether or not a particular over-all reaction is possible but also in interpreting reaction mechanisms and in aiding in a choice of catalysts for those mechanisms which seem most feasible.

The data of Figs. 1*B*, 1*F*, 1*G*, and 1*H* may be used to study the direct hydrogenation of acids to alcohols. For example:

$$\begin{aligned} CH_3CO_2H_{(g)} + 2H_2 &= C_2H_5OH_{(g)} + H_2O \qquad (6)\\ 2(-37{,}000) + 0 + \Delta F &= 2(-8{,}400) - 50{,}000 \text{ at } 400°\text{C.}\\ \Delta F &= +7{,}200 \text{ cal. at } 400°\text{C.} \end{aligned}$$

Although there is an actual free-energy increase indicated which is not very large, the reaction also proceeds with a decrease in volume so that equilibrium yields can be definitely helped by carrying out the reaction, at relatively high pressures (Table IX). The equilibrium yield is more favorable at lower temperatures, but here again the slower reaction velocity must be considered. Care must be exercised in the choice of catalysts so that they will have little, if any, dehydrating tendencies, and their hydrogenating ability must not be too violent (page 530); otherwise, the hydrocarbon rather than the alcohol will result as the product. These problems have been worked out, and the high-pressure hydrogenation of acids or, more particularly, their simple esters, which are more volatile, is a successful commercial process.

Temperature.—For the most part, the temperature for hydrogenation reactions is usually below 400°C., except in reactions where pyrolytic decomposition occurs concurrently with the hydrogenation reactions. In these cases, the temperature may extend to 500°C. Temperature is one of the most important variables affecting a reaction. *Practically every hydrogenation reaction can be reversed by increasing temperature.* It becomes necessary, then, to work at as low a temperature as possible where the rate of reaction will still be satisfactory. Whereas catalysts affect only the speed and course of a reaction, temperature affects the equilibrium position, the speed, and the path, or course, of a reaction. In general, then, increasing temperature adversely affects the equilibrium position, so that the maximum ultimate yield is decreased; but it affects favorably the speed of a reaction, so that in a given time, a greater quantity of product can be obtained. It becomes necessary to balance the less favorable equilibrium position with the faster rate of reaction. Fortunately, in recent years, the knowledge of catalysis has been so extended that satisfactory reaction rates are possible at lower temperatures where a more favorable equilibrium position prevails.

In some cases, an increase in temperature may adversely affect a catalyst, so that the reaction rate is decreased or reduced to practically nothing. These are the cases known as *sintering* of the catalyst; *i.e.*, the highly extended and porous surfaces of the catalysts are in some way collapsed or fused together so that the efficiency of the catalyst is seriously reduced. Here, again, a study of promoters, or substances that catalyze or accelerate the activity of a catalyst, may surmount the difficulties due, at least in part, to sintering.

Finally, a statement is necessary concerning the temperature coefficient of hydrogenation reactions. Barring decrease in activity of the catalyst (such as sintering), few if any hydrogenation reactions fit the generalized statement that the speed of a reaction may be doubled for every 10 to 15°C. increase in temperature. It usually takes 50°C. or more to double the speed of a hydrogenation reaction.

In general, the noble metal catalysts, such as platinum or palladium, are used from room temperatures to 150°C.; catalysts of the nickel and copper type, from 150 to 250°C.; and various combinations of metals and metal oxides, from 250 to 400°C.

Pressure.—Pressure, like temperature, can affect the rate of reaction as well as the equilibrium position. The rate of reaction is generally increased by increasing pressure, because a gas phase is usually present, and increased pressure gives increased concentration. In general, increased concentration speeds up a reaction. Pressure increases the equilibrium yield in a hydrogenation reaction when there is a decrease in the volume of the reaction as it proceeds. This is the simple application of the mass-action law, or LeChatelier's principle. In hydrogenation reactions, there is usually a decrease in volume.

Thus, pressure would have a greater effect on equilibrium yield in the reaction

$$CO + 2H_2 \leftrightharpoons CH_3OH$$

than in the reduction of formaldehyde

$$CH_2O + H_2 \leftrightharpoons CH_3OH$$

for the change in volume is greater in the first case. In simple cases, the effect of pressure on the equilibrium yield can be quantitatively estimated from application of mass-action principles.

The effect of pressure on the reaction rate is not subject to any definite quantitative laws. The results of one reaction may not occur in another. The point is best settled by experimental data. In general, however, increased pressure will result in an increased reaction rate. Thus, Brochet observed that phenol is hydrogenated very slowly at 150°C. at atmospheric pressure using a nickel catalyst but that at

15 atmos. at the same temperature the reaction was complete and rapid.[1] Maxted and Armstrong and Hilditch observed the velocity of hydrogenation to be proportional to the pressure.[2,3] Armstrong reported that the speed of hydrogenation of pyridine to piperidine varied as the square of the hydrogen pressure.[4] In the hydrogenation of acetone to isopropyl alcohol with identical batches of a copper chromite catalyst, Adkins and Connor observed the following conversions in reactions of ½ hr. duration.[5]

TABLE XIII.—EFFECT OF PRESSURE IN THE HYDROGENATION OF ACETONE

Pressure, Atmos.	Conversion, %
35	17
148	70
212	95

Again, Folkers and Adkins found that an increase in pressure from 100 to 200 atmos. increases the rate of hydrogenation of ethyl laurate to lauryl alcohol sevenfold and an increase in pressure from 100 to 300 atmos. increases it twenty-eightfold.[6] Results of hydrogenating acetoacetic ester, benzène, phenol, and aniline at various pressures have also been reported,[7] and there are many other references in the literature pointing to the general conclusion that an increase in pressure usually gives an increased rate of reaction. In general, then, the conclusion that increased pressure results in increased rate of reaction appears well substantiated.

There may be cases, however, where pressures below atmospheric are desirable, particularly when the reaction may need to be stopped at some intermediate stage of hydrogenation. Thus, Grignard observed, in hydrogenating at pressures less than atmospheric with nickel, copper, and platinum catalysts, that hydrogenations could be stopped at the first stage.[8] Phenol was reduced to cyclohexenol; benzaldehyde, to benzyl alcohol; benzonitrile, to benzaldimine; and phenylacetonitrile, at about 220 mm. pressure and 200°C., to phenylacetaldimine.

Time.—The time necessary for a hydrogenation reaction may vary from a few seconds to several hours, depending on the materials being hydrogenated, the catalyst, the temperature, and the pressure. In general, the more reactive the compound the faster the hydrogenation reaction. Thus, simple aldehydes are hydrogenated very readily, whereas the reduction of aromatic rings to saturated cyclic compounds or of esters to alcohols is a slower reaction. The type of apparatus or equipment used will depend on the speed of hydrogenation and *vice versa*. The usual type of bomb reactor is admirably suited to slow reactions, while an apparatus where the materials can be continually passed over the catalyst is best for fast reactions.

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[1] BROCHET, *Bull. soc. chim.* (4), **15**, 588 (1914); *Compt. rend.*, **158**, 1352 (1914).

[2] MAXTED, *J. Soc. Chem. Ind.*, **40**, 169T (1921).

[3] ARMSTRONG and HILDITCH, *Proc. Roy. Soc.*, **100A**, 240 (1921).

[4] ARMSTRONG, Lecture before the British Institute of Chemical Engineers, Oct. 30, 1931.

[5] ADKINS and CONNOR, *J. Am. Chem. Soc.*, **53**, 1093–1095 (1931).

[6] FOLKERS and ADKINS, *J. Am. Chem. Soc.*, **54**, 1153 (1932).

[7] ADKINS, CRAMER, and CONNOR, *J. Am. Chem. Soc.*, **53**, 1403 (1931).

[8] GRIGNARD, *Bull. soc. chim. Belg.*, **37**, 41 (1928).

The Ratio of Hydrogen to the Substances Being Hydrogenated.—The ratio of hydrogen to the substance being hydrogenated is conveniently expressed in terms of partial pressures. It frequently happens that the speed or path of a certain hydrogenation can be affected by the proportion of hydrogen to the substance. Although no extensive data on this phase of hydrogenation are available in the literature, it has been found that ethyl lactate and malonate are reduced to the corresponding alcohols in good yields in a flow system at pressures of about 1,300 lb. per sq. in., where practically the entire pressure is hydrogen and the partial pressure of the esters only a few centimeters. Similar results are obtained in the course of other hydrogenations.[1] Usually, such hydrogenations are carried out at considerably higher total pressures, *viz.*, about 3,000 lb. per sq. in. In the examples previously cited, the higher total pressure was lessened, and a higher ratio of hydrogen pressure to the partial pressure of the substance being hydrogenated was employed. This method of operation is, however, somewhat different from that usually employed.

Liquid- or Gas-phase Reactions.—The hydrogen, the substance being hydrogenated, and the product of hydrogenation may exist entirely in the gas phase, or the substance and the product may exist as a liquid phase. In this latter case, the hydrogen is in contact with the substance, either as a gas phase above or dissolved in it. Hydrogenation reactions obviously cannot occur without intimate contact of the hydrogen with the reacting substance and the catalyst. The type of reaction may differ, depending on whether the hydrogenation is in the gas phase or the liquid phase. Thus, Lush found, in hydrogenating naphthalene, using a nickel catalyst, that tetralin was the principal product formed in the vapor-phase reaction whereas decalin was produced by the liquid-phase hydrogenation.[2]

In liquid-phase reactions, there must be opportunity for intimate contact of hydrogen with the substance being hydrogenated and the catalyst. This is usually accomplished by some means of shaking, by stirring, or by circulating hydrogen through the liquid. Another factor that greatly facilitates intimate contact is the solubility of hydrogen in the substance undergoing hydrogenation. Increased pressure favors greater solubility of hydrogen, and an intimate contact comparable to gas-phase reaction is thus possible. The principal difference is the ratio of hydrogen to the substance being hydrogenated. In the gas phase, this ratio may be varied over a very wide range, but, in the liquid phase, it is governed by the solubility of hydrogen.

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[1] TRENT, Unpublished results, Penn. State Coll. (1933).

[2] LUSH, *J. Soc. Chem. Ind.*, **26**, 454T (1927).

Solubility of Hydrogen.—The effect of the solubility of hydrogen in the reacting substance obviously relates only to liquid-phase reactions. As indicated above, an increase in the pressure of hydrogen increases the solubility in a given liquid, and it has been found that this increase in solubility with pressure follows Henry's law with reasonable accuracy at ordinary temperatures in various liquids, such as methanol, isopropanol, paraffin hydrocarbons, and heavy oils.[1] However, it does not follow that the solubility of hydrogen in liquids will decrease with increasing temperatures, as might be expected. Thus, Grimm, in discussing the catalytic hydrogenation of coal and oil, states that the solubility of hydrogen in oils increases with the temperature, it being three times as great at 300 as at 20°C.[2] The solubility of hydrogen in liquids undoubtedly plays an important, if not the principal, role in liquid-phase hydrogenations.

The Exothermic Character of the Hydrogenation of Reaction.—The values for the heat of reaction are generally obtained from thermochemical data, when data relating specifically to the problem are not available. Depending on the type of hydrogenation reaction, varying amounts of heat may be liberated. Hydrogenations are usually exothermic, and, since the reaction occurs only because of the catalyst, local temperatures in the surfaces of the catalyst may reach surprisingly high values. These not only tend to divert the reaction to side reactions such as cracking but are likely to impair the efficiency of the catalyst because of sintering, which is the collapse of the active catalytic surface due to excessive heat. In problems of commercial design, the exothermic character of the reaction must consequently be given careful attention. Uncontrolled temperatures not only influence the course of the reaction and diminish the efficiency of the catalyst but also necessitate materials of construction that can withstand the maximum conditions of temperature and pressure likely to occur. In large units, temperature control is usually best obtained through proper heat interchange with the incoming materials.

V. GENERAL PRINCIPLES CONCERNING HYDROGENATION CATALYSTS

Catalysts are essential to most hydrogenation reactions. Very few hydrogenations occur in the absence of some sort of catalyst. These cases of noncatalytic reactions may happen when another reaction is occuring along with the hydrogenation reaction, so that extremely active or liberated hydrogen is available from this other reaction in limited amounts. In other cases, the reaction temperature may be high where, in addition to hydrogenation reactions, pyrolytic or cracking reactions are also occuring so that hydrogen gas in the absence of catalysts can add to the molecular fragments produced by the cracking. Thus, the earlier work of Bergius on coal hydrogenation was noncatalytic, but later the process became practically entirely catalytic through the developments of the I. G. Farbenindustrie in Germany.

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[1] Frolich, Tauch, Hogan, and Peer, *Ind. Eng. Chem.*, **23**, 548 (1931)

[2] Grimm, *Intern. Conf. Bituminous Coal*, II, 49 (1931).

Excepting these few instances, the large bulk of hydrogenation reactions use hydrogen gas as the source of hydrogen, and the function of the catalyst is to effect the over-all result of chemically combining the gaseous hydrogen with the substance capable of adding hydrogen to its molecular structure. It is the purpose of the catalyst to effect this combination along the desired path as quickly as possible. The following brief discussion is intended to clarify some of the essential features of a catalyst.

Surface.—For the most part, hydrogenation catalysts are solids consisting of metals and metal oxides. The hydrogenation is effected at the surface of the catalyst, so a highly extended surface is essential. However, a catalyst surface differs considerably from that produced by simply an extensive mechanical subdivision of matter. Taking a piece of bar nickel or copper and subdividing it mechanically to pass, say, a 50-mesh sieve would not produce an active nickel or copper catalyst. Usually, the preparation of a catalyst is associated with some chemical reaction whereby a highly extended, porous, and honeycombed surface is produced so that the density of the surface metal is far less than that of the bulk metal. Certain surface atoms may become so removed from other adjoining ones that they may approach a gasified state, at conditions far removed from the normal vaporization of the metal. Certain valence bonds of these atoms which normally would be shared with other atoms in the usual dense metallic state are freed, and here is believed to lie the reason for the catalyst's activity. These surface atoms, having varying degrees of unsaturation compared with the bulk metal or metal oxide, will strongly adsorb other substances with which they may come in contact, and active catalysts usually have high adsorptive powers. Although adsorption is closely related to the successful performance of a catalyst, it may ruin an active catalyst, because other substances called catalyst poisons may be so strongly retained by these active atoms that the substance being hydrogenated can no longer reach the active or catalytic areas.

The speed of a hydrogenation will depend on the type and amount of active surface available. Increasing the ratio of catalyst to the substance undergoing hydrogenation usually increases the speed of the hydrogenation, although not necessarily in direct proportion to the increase in amount of catalyst. In batch operations, the catalyst usually is from about 1 to 10 per cent by weight of the substance being hydrogenated. Following are some data of Carothers and Adams on the hydrogenation of benzaldehyde with varying amounts of the same batch of a platinum oxide-platinum black catalyst.[1] In each experiment, 21.2 gm. of benzaldehyde was used and dissolved in 50 cc. of alcohol.

Grams of Catalyst Used	Time for Complete Hydrogenation
0.0288	5.5 hr.
0.0575	60 min.
0.115	34 min.
0.23	23 min.

Mixed-metal Catalysts.—Because an apparently small and inappreciable amount of substance might impair or poison the activity of a catalyst, strenuous efforts must be made to prepare the catalyst as nearly chemically pure as possible. But it will usually be found that, in this state, activity is either nil or very low. The solution to this dilemma is to recognize more clearly the class of substances to which poisons and promoters belong. Catalyst poisons are usually substances that can react chemically with the catalyst or else, because of their volatility, can condense on to and blot out the active areas of the catalyst. The common poisons are halogens, sulfur, arsenic, and sometimes metals of low melting point such as mercury, lead, and tin.

Promoters, or substances that increase a catalyst's activity, are usually quite stable and frequently exist in physical combination with the catalyst. It frequently happens that they themselves are catalysts for the same or a similar type of reaction. Thus, a small amount of chlorine or sulfur will render a copper catalyst used for the dehydrogenation of methanol entirely inactive,[2] whereas the addition of about 3 per cent of zinc oxide to a pure copper catalyst, when used under exactly the same conditions, will increase the activity threefold.[3]

In those cases where some of the more common poisons, such as sulfur, have to be tolerated, it is possible to utilize catalysts that contain sulfur. The molybdenum sulfides are examples of catalysts of this type. Under proper temperature and pressure conditions, these materials are effective hydrogenation catalysts.

The use of mixed-metal catalysts or promoted catalysts has been rapidly extended in recent years. More common mixtures with the well-known types of catalysts are nickel-copper, nickel-alumina, copper-zinc oxide, copper-chromium oxide, and zinc oxide-chromium oxide. However, the recent chemical and patent literature describes the use of combinations of practically every metal and metal oxide in the periodic system.[1,2]

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[1] Carothers and Adams, *J. Am. Chem. Soc.*, **45**, 1071 (1923).

[2] Frolich, Fenske, Perry, and Hurd, *J. Am. Chem. Soc.*, **51**, 187 (1929).

[3] Frolich, Fenske, and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).

Stability.—The period of activity of a catalyst is a rather indefinite thing. This is because such activity depends not only on the nature of the materials brought in contact with it but also on the stability and permanence of the active areas, which most likely are responsible for the functioning of the catalyst. Loss in activity from contamination with foreign materials is best characterized as poisoning. Loss in activity from a collapse and aggregation of the highly distended surface is best termed sintering. It should be remembered that a catalyst, like any other system, is striving to reduce its surface energy to a minimum for just the same reasons that a droplet of water forms a sphere. Thus, there is always a force tending to bring about the collapse of the extended surface, with the result called sintering. A function of promoters is to maintain and prolong the existence of the active areas of a catalyst.

It is sometimes possible to reactivate a catalyst that has lost its activity, especially when the loss in activity is due to some adsorbed materials. Passing hydrogen alone over the catalyst for a period of time may help; or in some cases, it is possible to reactivate the catalyst by passing a small amount of oxygen over it. In these cases, the adsorbed materials are probably burned off. Oxygen was found to reactivate catalysts used in the synthesis of methanol from carbon monoxide and hydrogen[3] but quite effectively to poison an iron catalyst used in the synthesis of ammonia.[4]

Usually, catalysts of a very high initial activity are short-lived, and it becomes necessary to choose between a high initial rate of hydrogenation and a somewhat lower but better average rate, such as is obtained in a stable catalyst. These stable catalysts are often obtained through the use of mixed-metal or promoted catalysts where the active areas are large. In addition, the mixtures of metals and metal oxides usually afford the best protection against sintering. Then by careful elimination of any foreign materials in the reactor, in the hydrogen, or in the substance being hydrogenated, a reasonable period of catalyst activity can be assured.

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[1] Berkman, Morrell, and Egloff, "Catalysis," pp. 809–888, Reinhold Publishing Corporation, New York, 1940.

[2] "Twelfth Catalysis Report," National Research Council, pp. 114–117, John Wiley & Sons, Inc., New York, 1940.

[3] Fenske and Frolich, *Ind. Eng. Chem.*, **21,** 1052 (1929); Nussbaum and Frolich, *Ind. Eng. Chem.*, **23,** 1386 (1931).

[4] Almquist and Black, *J. Am. Chem. Soc.*, **48,** 2815 (1926).

The catalyst's life in industrial processes may extend from a month to a year or more; *i.e.*, the catalyst is active for this period, after which it becomes necessary to remove it from the reactor and replace it with fresh material or otherwise to recondition it chemically. However, it is relatively common practice to rejuvenate catalysts periodically be removing deposits, poisons, or other adsorbed and undesirable materials. This is usually accomplished by passing air, steam, or other reactivating gas over the catalyst without removing it from the reactor. The periods between rejuvenation may range from a day or less to months.

Preparation.—Hydrogenation catalysts can be prepared in practically an unlimited number of ways. However, there are again certain generalized or fundamental steps that are quite common to the preparation of any active catalyst. These principles are intended to serve as a guide to catalyst preparation when other more definite information is not available. It may be found later that certain of these steps are not necessary or are relatively unimportant. However, it is believed that if they are recognized, a higher average success in catalyst preparations will result. The five most important principles are as follows.

1. To ensure the production and duplication of a reasonably active catalyst, relatively pure materials should be used in its preparation. Because of the small amounts of a substance that may act as either a poison or a promoter, the purity of the starting chemicals should be known; this will be the difference between the building up of successful catalysts by hit-or-miss methods and by a rationalized procedure.

2. Generally the better practice is to prepare the catalyst through a chemical reaction rather than by a mere physical or mechanical method. Thus, in the preparation of a nickel catalyst, it is far better to prepare it by precipitation of nickel hydroxide from nickel nitrate and alkali and reduce the hydroxide to oxide and to metallic nickel by hydrogen than to prepare it by subdividing a nickel bar. A finer and more active state of subdivision together with a greater possibility of reproduction of the catalyst generally results by applying rather simple and definitely known chemical reactions.

In mixtures of metal and metal oxide catalysts, generally anything that can be done to promote or bring about more intimate contact between the materials will result in an improved catalyst. Although this may be obvious, sometimes it may not be fully appreciated. This point may be illustrated in the preparation of copper-zinc oxide catalysts.[1] If the efficiency of the coprecipitated hydroxides of copper and zinc is rated as 100, other methods of preparation compared as follows when studying the decomposition of methanol:

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[1] FROLICH, FENSKE, and QUIGGLE, *Ind. Eng. Chem.*, **20,** 694 (1928).

TABLE XIV.—EFFECT OF METHOD OF PREPARATION ON CATALYST EFFICIENCY

Method of Preparation	Decomposition Efficiency, %
1. Hydroxides precipitated together	100
2. Hydroxide gels mixed	83
3. Zinc hydroxide precipitated on suspended copper hydroxide	75
4. Calcined nitrates	70
5. Copper hydroxide precipitated on suspended zinc hydroxide	67

The activity of nickel catalysts supported on kieselguhr is dependent n the method of preparation,[1] and likewise the method of preparing opper oxide-chromium oxide catalysts affects their activity.[2]

3. Precautions should be taken in the course of the preparation of a atalyst to keep it free from any contaminating substances other than hose definitely desired in the catalyst. The catalyst should be prepared ust as any pure substance is; experience indicates that effort in this direction is well expended. When precipitation of the hydroxide or oxide may occur in the course of preparing a metal catalyst, it is desirable to use the nitrate of the metal and ammonium hydroxide as a precipitant when there are no other conflicting chemical reactions. In this way, any ammonium salts or excess hydroxide are easily volatilzed by careful heating.[3]

4. When it is necessary to reduce a catalyst prior to use, precautions must be taken in its reduction. It may be said that catalysts are either made or destroyed in this reduction operation. The reduction of metal oxides by hydrogen is generally exothermic; consequently, the catalyst's activity may be seriously impaired by sintering if reduction temperatures are uncontrolled. Careful measurement and regulation of the temperatures of reduction are important. Sometimes, it is advisable to use hydrogen diluted with nitrogen. In general, the temperatures of reduction should be no higher than necessary to effect a gradual and controlled reduction of the oxide. It is relatively easy to raise the catalyst temperature to incandescence and even to destruction of its activity through carelessness in controlling the temperature during reduction.

5. If the catalysts must be stored, it is generally better to store them in the more stable state. Thus, if the catalyst needs to be reduced prior to use, it is generally better practice to store the oxide and reduce batches of catalyst as needed. These are simple precautions which enable the catalyst to have its maximum activity when used. In addition, storage in containers free from materials that are liable to be poisons is obviously

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[1] COVERT, CONNOR, and ADKINS, *J. Am. Chem. Soc.*, **54,** 1652 (1932).

[2] FOLKERS and ADKINS, *J. Am. Chem. Soc.*, **54,** 1153 (1932).

[3] FROLICH, FENSKE, and QUIGGLE, *J. Am. Chem. Soc.*, **51,** 61 (1929).

necessary. Cork- or glass-stoppered bottles are preferable to rubber-stoppered ones, as there is danger of sulfur contamination from the latter.

General Classification of Hydrogenation Catalysts.—The number of catalysts capable of effecting hydrogenations is large; in addition, many types of hydrogenation are possible. Practically any type of unsaturation can be hydrogenated catalytically. It has been pointed out that hydrogenation may involve the saturation of a carbon-to-carbon linkage or the reduction of carbonyl or carboxyl or hydroxyl groups and may even involve the breaking of carbon-to-carbon linkages, as in the hydrogenation of coals and mineral oils. In general, however, hydrogenation catalysts may be classified as follows:

Vigorous Hydrogenation Catalysts.—These catalysts are usually characterized by the fact that they carry the hydrogenation to the greatest extent possible, so that the maximum addition of hydrogen to compound occurs under the particular operating conditions. Thus, in the case of simple aldehydes, the reduction will pass beyond the alcohol stage and end at the saturated hydrocarbon. Even here, the tendency to saturate the carbon atoms may be sufficiently great to cause cracking or to break the carbon-to-carbon bonds so that still more hydrogen can be added, the final result being the formation of the hydrocarbon with the greatest hydrogen-to-carbon ratio, *viz.*, methane. Cracking tendencies are usually associated with these violent hydrogenation catalysts, although through control of the variables of temperature and pressure, the cracking reactions can usually be suppressed. Common catalysts belonging to this class usually consist of the nickel, cobalt, or iron type and sometimes of molybdenum and tungsten oxides or sulfides.

Mild Hydrogenation Catalysts.—The term *mild* should not be confused with activity. These catalysts will effect hydrogenations just as rapidly as the violent hydrogenation types, but they are able to carry out only one step at a time in a hydrogenation, or at least they do not permit the reaction to proceed to the hydrocarbon stage. A great many catalysts belong to this class, and they are being developed rapidly. These catalysts will easily reduce an aldehyde or ketone to the alcohol, or an acid or ester to an alcohol. The large number of catalysts developed for the direct synthesis of methanol from water gas belong to this class, and they usually contain copper, zinc oxide, chromium oxide, and manganese oxide and may include some of the rarer elements as promoters. In addition, the noble-metal catalysts such as platinum or palladium or their oxides belong to this class.

Catalysts with Properties Other than Hydrogenation.—The synthesis of higher alcohols from water gas involves a condensation as well as a hydrogenation reaction. These so-called higher alcohol catalysts are usually of the mild hydrogenating type but contain some more alkaline naterials, such as sodium, calcium or barium carbonates, or aluminum r magnesium oxides. Other types of catalysts are capable of splitting ut water from a molecule along with the hydrogenation but do not ossess any appreciable cracking tendencies. These usually are of he vigorous hydrogenating type but contain considerable and even sometimes preponderating quantities of dehydrating catalysts, such s alumina, thoria, tungstic oxide, or chromium oxide. They can ffect such reductions as phenol to benzene and as cresols to aromatic hydrocarbons and convert various hydroxy compounds to hydrocarbons, with little or no other changes in the molecular structure.

VI. APPARATUS AND MATERIALS OF CONSTRUCTION

The trend in hydrogenation practice appears to be toward the use of higher pressures, where the apparatus is smaller. Under such conditions, the reaction velocity is increased; the equilibrium positions made more favorable; the reaction path better defined, with fewer side reactions; and heating and cooling and heat interchange are facilitated. The design and construction of equipment for high-pressure work are, however, somewhat more complicated than for low-pressure operations. Alloy steels are by far the most common materials of construction.

Reaction chambers or autoclaves are usually of two types, one in which the contents are agitated or stirred in some way and the other in which the reactor and contents are stationary. The first is used with materials such as solids or liquids to bring intimate contact among the catalyst, the material, and the hydrogen. The second type is used where the substance may have sufficient vapor pressure at the temperature of operation so that a gas- as well as a liquid-phase reaction is possible. It is also most frequently used in continuous operation where larger quantities of material need to be processed than can be done conveniently with batch or autoclave methods. In this case, the reacting material, if liquid, is passed along with hydrogen over the catalyst. A drawing of a small, experimental-scale, stirred autoclave is shown in Fig. 2. Here the packing around the stirrer is water cooled to facilitate a tight joint. Figure 3 shows a small-scale type of agitated reaction vessel in which the entire reactor is rocked through a sufficient angle to give intimate mixing of the contents.

A convenient small-scale unit is shown in Fig. 4, page 533. The material to be hydrogenated, if a liquid, is fed into the small, high-pressure pump—or, if a solid, it is dissolved in a suitable solvent. All that the pump needs to do is to put sufficient pressure on the liquid to raise it to the pressure on the reactor. Since liquids are relatively incompressible, the work expended in this operation is small. The material is heated near the inlet end of the reactor to the reaction temperature, and then it flows along with the hydrogen over the catalyst contained in the middle or latter half of the reactor. It simply flows or vaporizes through the reactor, the time of contact with the catalyst being dependent on the rate of pumping. Small, high-pressure proportioning pumps are readily available, which enable the rate of flow to be accurately maintained as well as readily varied. At the exit end of the reactor, the liquid is condensed, and a trap allows it to be withdrawn from the system without undue loss of hydrogen. Instead of dropping the hydrogen pressure down to substantially atmospheric pressure to measure the amount passing over the catalyst per unit volume or per mole of material being hydrogenated, it is measured at full operating pressure by determining the amount of water displaced from the hydrogen-control tank on the right. This gives an accurate control and measure of the hydrogen

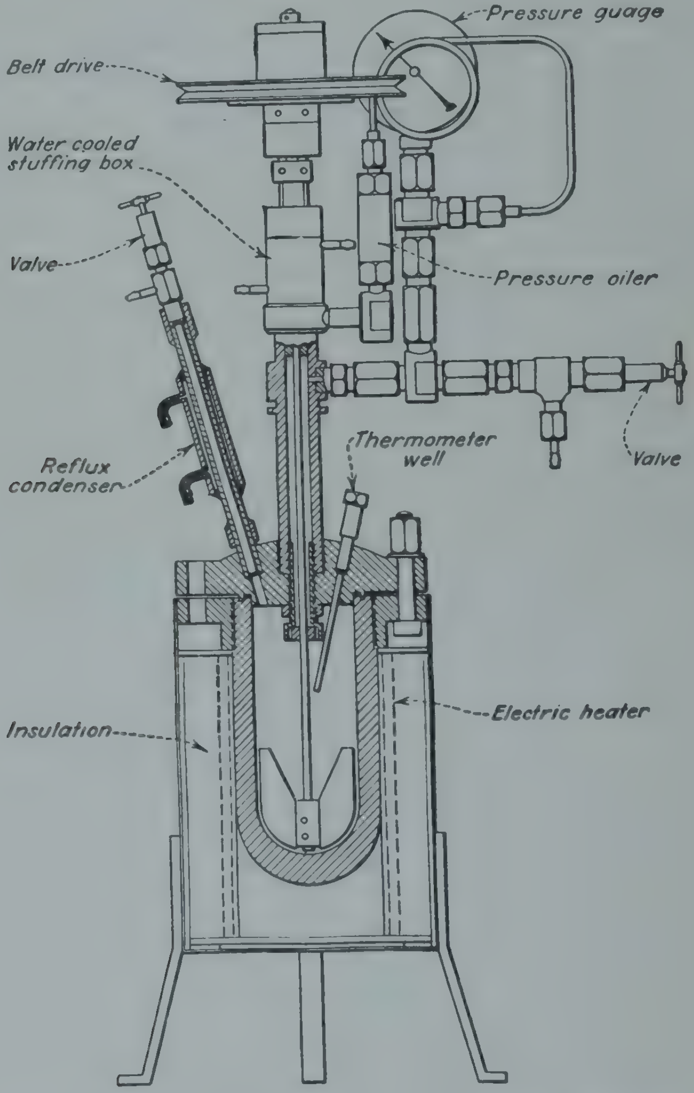
Pressure guage
Belt drive
Water cooled stuffing box
Valve
Pressure oiler
Thermometer well
Valve
Reflux condenser
Electric heater
Insulation

Fig. 2.—Diagrammatic sketch of high-pressure autoclave.

passed over the catalyst and avoids reducing the hydrogen pressure with a corresponding loss of hydrogen. With the use of a two-unit proportioning pump, water can be pumped into the hydrogen-control tank to bring it

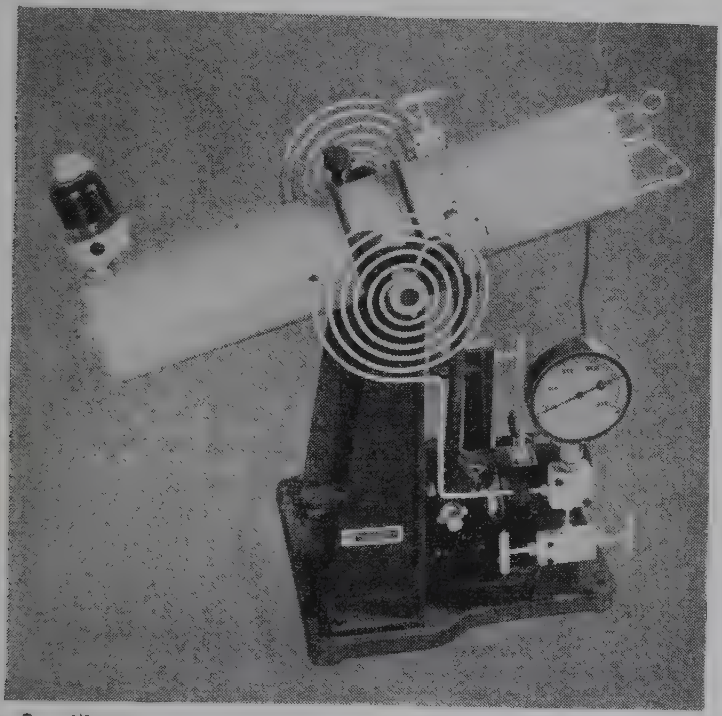

FIG. 3.—Shaking autoclave for pressures to 15,000 lb. per sq. in.

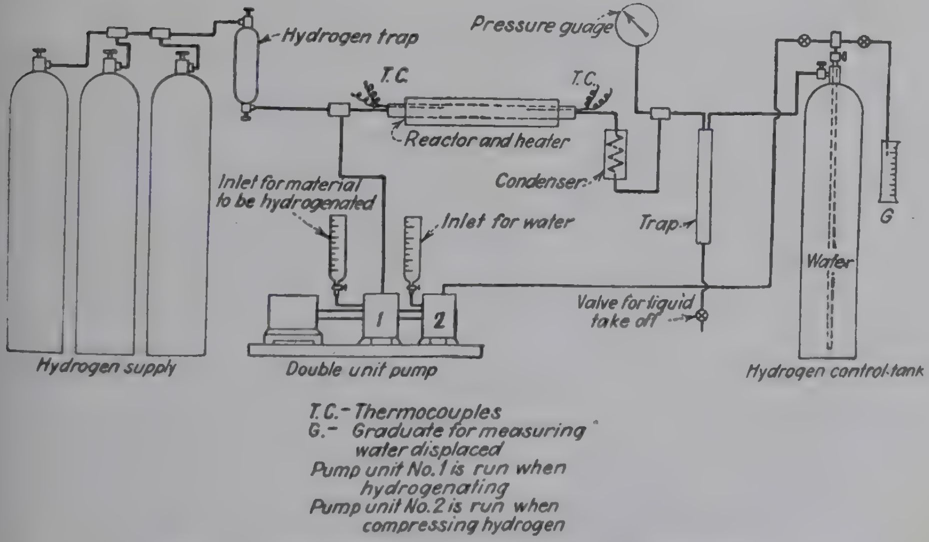
Hydrogen trap
Pressure guage
T.C.
T.C.
Reactor and heater
Inlet for material to be hydrogenated
Condenser
Inlet for water
Trap
G
Water
Valve for liquid take off
1
2
Hydrogen supply
Double unit pump
Hydrogen control-tank
T.C.- Thermocouples
G.- Graduate for measuring water displaced
Pump unit No. 1 is run when hydrogenating
Pump unit No. 2 is run when compressing hydrogen

FIG. 4.—Flow-system apparatus for hydrogenations.

back to pressure and thus make up for the hydrogen consumed in the reaction. In this way, by careful working, the hydrogen lost is practically only that which is consumed in the reaction. It is also important to note hat in this operation the ratio of hydrogen to the substance being hydrogenated is very large. This facilitates the hydrogenation reaction. The substance may flow through the reactor at only a fraction of an atmosphere partial pressure, whereas the partial pressure of hydrogen may be 100 or 200 atmos. It has been found that hydrogenations in this type of setup proceed very satisfactorily at considerably lower pressures than when operating in a batch or autoclave type of apparatus. This is undoubtedly because the higher total pressure has been in part replaced by a higher ratio of the partial pressure of hydrogen to the partial pressure of the substance undergoing reduction.

In the operation of large units, heating of the ingoing materials is best accomplished by heat exchange with the outgoing materials and adding additional heat by means of high-pressure pipe coils. A pipe coil is the only convenient and efficient method of heating, for the reactor is usually so large that the heating of it is very difficult. It is usually better practice to add all the heat needed to the materials before they enter the reactor and then simply have the reactor properly insulated thermally. Hydrogenation reactions are usually exothermic, so that once the process is started, the problem may be one of heat removal. This is accomplished by allowing the heat of reaction to flow into the ingoing materials, by heat exchange in the reactor, or, if it is still in excess, by recycling and cooling in heat exchangers the proper portion of the material to maintain the desired temperature.

VII. INDUSTRIAL PROCESSES

Of the many industrial applications of hydrogenation, only four will be described here: (1) The hydrogenation or hardening of vegetable or marine oils; (2) the synthesis of methanol, higher alcohols, and hydrocarbons from water gas; (3) the reduction of long-chain fatty acids to alcohols, and (4) the hydrogenation of hydrocarbons, mineral oils, and coal. These four processes cover a wide variety of catalysts used in hydrogenation reactions; they deal with the processing of raw materials in the form of solids, liquids, and gases; and they employ practically the entire range of pressures and the temperatures used in any sort of hydrogenation. Finally, each of these four processes is an application of one of the four types of hydrogenation discussed at the beginning of this chapter.

Hydrogenation or Hardening of Fats.—The purposes of the hydrogenation of vegetable and animal oils are (1) to produce a hard fat or one of greater consistency than the original liquid oil and (2) to remove certain impurities that are not removable by any other means, thus rendering the oil useful for purposes for which it could not otherwise be adapted. The process is essentially one of converting the glycerides of the unsaturated fatty acids into glycerides of saturated acids; thus, in the case of olein, the addition of 6 atoms, or only 0.68 per cent by weight of hydrogen, converts it into stearin:

$$(C_{17}H_{33}\cdot CO\cdot O)_3C_3H_5 + 3H_2 \rightarrow (C_{17}H_{35}\cdot CO\cdot O)_3C_3H_5$$

The reaction is carried out at temperatures from 100 to 250°C. (212 to 480°F.), at pressures usually less than 200 lb. per sq. in., with nickel as a catalyst. The processing of edible oils is usually carried out with considerable care and at lower temperatures in order to minimize undesirable side reactions.

A variety of oils may be used in the process. There are glycerides not only of oleic acid but also of linoleic acid, the latter containing two double bonds instead of one, as in oleic acid. Furthermore, there are a number of isomeric *oleins*, where the unsaturation is at different points in the long chain of carbon atoms. Each of these compounds or isomers behaves a little differently from the others on hydrogenation. In the case of marine oils, fatty acids of from 14 to 24 carbon atoms are known to be present. Table XV gives an approximate analysis of several of the more commonly used oils,[1] and Table XVI pertains to the composition of whale oil.[2]

TABLE XV.—PERCENTAGE COMPOSITION OF OILS USED IN HARDENING PROCESSES

Composition or property	Peanut	Cotton-seed	Corn	Soybean	Linseed
Oleic acid, %	50–70	23–33	45–49	21–34	21–38
Linoleic acid, %	13–26	39–48	34–41	49–59	3–23
Linolenic acid, %	Nil	Nil	Nil	2–8	26–58
Myristic acid, %	Nil	0.3–2	2	Nil	Nil
Palmitic acid, %	6–9	19–23	8–11	6–10	4–7
Stearic acid, %	2–6	1–3	2–4	2–4	2–5
Arachidic acid, %	2–5	0.1–1	0.4	0.7–1	0.2–1
Lignoceric acid, %	2–3	Nil	0.2	0.1	0–0.4
Unsaponified matter, %	0–0.3	0.9	2	0.6	0.5–2
Smoke point, °F	464	508	440	492	320
Fire point, °F	692	644	678	673	680
Flash point, °F	632	582	618	618	588
Iodine value	83–95	103–115	116–130	103–152	170–204

When these oils are completely hydrogenated, solids result; and when the oils are partially hydrogenated, fats of various consistencies or melting points are obtained. The degree of hydrogenation is readily determined for any given oil by the melting point, iodine-absorption number, or

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[1] *Chem. Eng. News*, **23**, No. 13, 1169 (1945).

[2] RICHARDSON, KNUTH, and MILLIGAN, *Ind. Eng. Chem.*, **17**, 80 (1925).

TABLE XVI.—PERCENTAGE COMPOSITION OF FATTY ACIDS OF WHALE OIL

Material	%
C_{14} acids, myristic	4.5
C_{12} acids, palmitic	11.5
palmitolic	17.0
C_{18} acids, stearic	2.5
unsaturated (nearly all oleic)	36.5
C_{20} acids; unsaturated	16.
C_{22} acids; unsaturated	10.
C_{24} acids; unsaturated	1.5
Unsaponifiable material	0.7

refractive index. The following table (XVII) gives the melting points of some hydrogenated products.[1]

TABLE XVII.—MELTING POINTS OF COMPLETELY HYDROGENATED OILS

Oil	M.p., °C.
Coconut	43 to 45
Whale	52 to 56
Cottonseed	62 to 63
Olive	68 to 69
Soybean	69 to 71
Castor	86 to 90

The process of hydrogenating a mixture of olein with more unsaturated glycerides such as linolein is selective; *i.e.*, the linolein, or fatty acids containing two double bonds, is practically entirely converted into olein before this, in turn, is hydrogenated to stearin. In other words, during the hydrogenation of the more highly unsaturated oils, it passes through a stage where it is practically equivalent to an oleinic oil before it proceeds to complete saturation. This technic is also employed in the selective hydrogenation of small amounts of linoleic and linolenic acid constituents of tallow soaps that are to be used in conjunction with the production of butadiene-styrene copolymers.

This selectivity is not so apparent in the hydrogenation of whale and menhaden oils. In the hardening of these oils, a more abrupt change occurs at an iodine value of about 84, at which time nearly all the acids of more than two double bonds have disappeared. Below this point, hydrogenation results both in the formation of saturated acids and in the conversion of the C_{20} and C_{22} acids containing two double bonds to corresponding acids of one double bond. Thus, the hydrogenation of these marine oils is different from that of typical vegetable oils, in which substantial increases in the quantity of saturated acids present is coincident with the almost complete disappearance of acids containing more than one double bond.[2]

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[1] HILDITCH, "Catalytic Processes in Applied Chemistry," p. 226, D. Van Nostrand Company, Inc., New York, 1929.

[2] RICHARDSON, KNUTH, and MILLIGAN, *Ind. Eng. Chem.*, 17, 80 (1925).

The oils to be hydrogenated should be reasonably free from materials likely to poison the catalyst. Impurities that may be present and that are poisonous to nickel, in decreasing order of toxicity, are organic sulfur compounds; oxidized unsaturated fatty compounds; colloidal suspensions of protein, of mucilage, etc.; moisture; and free higher fatty acids. Free fatty acids, up to about 3 per cent, do not seriously interfere. Moisture should preferably be kept low, because certain nickel catalysts tend to adsorb water in preference to oils, and, in the preparation of palatable oils, moisture is apt to produce undesirable materials through saponification. Organic sulfur compounds, although difficult to remove, are fortunately very seldom present in amounts likely to impair seriously the activity of the nickel. Oxidized materials and other colloidal and high-molecular-weight compounds can be removed either with an aqueous alkali wash or by adsorption, using certain earths or charcoals.

Nickel is by far the most commonly used catalyst in oil hardening. The catalyst problem consists of three phases: (1) preparation of a suitable catalyst; (2) the maintenance of its activity as long as possible; and (3) the recovery and reactivation of the spent catalyst. Nickel catalysts are of different types, depending upon the operation in which they are used. They may be in a relatively fine state, particularly in those processes where stirring or other agitation of the oil is used, or they may be supported on inert materials such as clays, kieselguhr, charcoal, or pumice, which extend the surface of the catalyst and facilitate the filtration of the catalytic mass from the oil. The decomposition of nickel formate produces a finely divided, active, and practical catalyst.[1] Finally, in continuous processes, the nickel may be in a massive form, *i.e.*, as turnings, wool, or screen which has previously been activated by special processes involving alternate oxidation and reduction to produce an active nickel surface.

There are numerous patents pertaining to apparatus and processes for hydrogenating oils. For the most part, these may be divided into three types: (1) a vessel nearly full of oil containing the catalyst in suspension through which hydrogen is circulated by mechanical means, possibly also with circulation of the oil to maintain the suspension of the catalyst; (2) a vessel full of hydrogen and oil in which an intimate mixture is attained without moving parts, or stirrers; and (3) continuous processes in which the catalyst is maintained stationary and through which oil and hydrogen are continuously circulated.

Apparatus belonging to the first type is shown in Fig. 5. It consists of a cylindrical tank, containing a helicoid or spiral propeller, driven by a pulley. Hydrogen is admitted through a perforated pipe, and internal coils provide ample means for heating or cooling the charge of oil contained in the vessel.[1]

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[1] WURSTER, *Ind. Eng. Chem.*, **32**, 1193 (1940).

Another apparatus pertaining to the second type is shown in Fig. 6. Here there are no moving agitators and consequently no stuffing boxes to leak.[2] This apparatus is built in various sizes, sometimes 20 to 30 ft. tall. The essential features are intimate contact of the liquid and gas phases and the maintenance of this intimate contact over as large a portion of the whole bulk of oil as is practicable. The catalyst is suspended in the oil in a finely divided state. The oil and gas flow countercurrently through the tall mixing column, intimate contact being caused by the action of fixed propellerlike baffle plates, causing the oil and gas mixture to rotate alternately in opposite directions. In addition, the inclination of the baffles is such that they exert, along with the rotating motion, such an action on the hydrogen-oil mixture that this is alternately thrown toward the center of the column and its periphery.

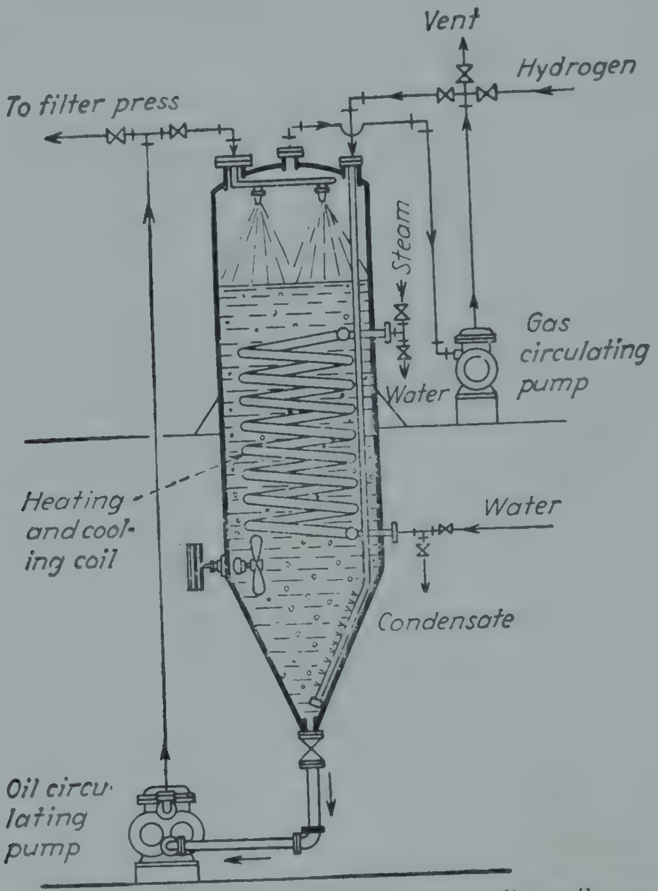

FIG. 5.—Oil-hydrogenating unit with internal heating and cooling coil, gas-circulating pump, oil-and-catalyst-circulating pump, and propeller-type mechanical agitator.

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[1] WURSTER, *loc. cit.*

[2] MAXTED, U. S. 1,313,407 (1919).

In operation, the column (Fig. 6) is filled with oil. It enters at the top and is recirculated by the pump. The enlarged section at the top serves to effect a separation of the intimate hydrogen-oil mixture so that hydrogen may be withdrawn at the top of the apparatus, repressured by the gas compressor, and then returned at the bottom of the column. The degree of mixing of hydrogen and oil may be varied by the rate at which the gas compressor and oil pump operate. A steam jacket serves to heat the charge and maintain suitable temperatures. This process is said to effect very rapid hydrogenation, for instance, of peanut or cottonseed oil, in from 15 to 25 min., with an initial temperature of 130°C. Because of the rapid reaction at low temperature, this process is particularly applicable to hardening of oils for edible purposes, where the product must possess a good flavor. The usual working pressure is about 60 lb. per sq. in.[1]

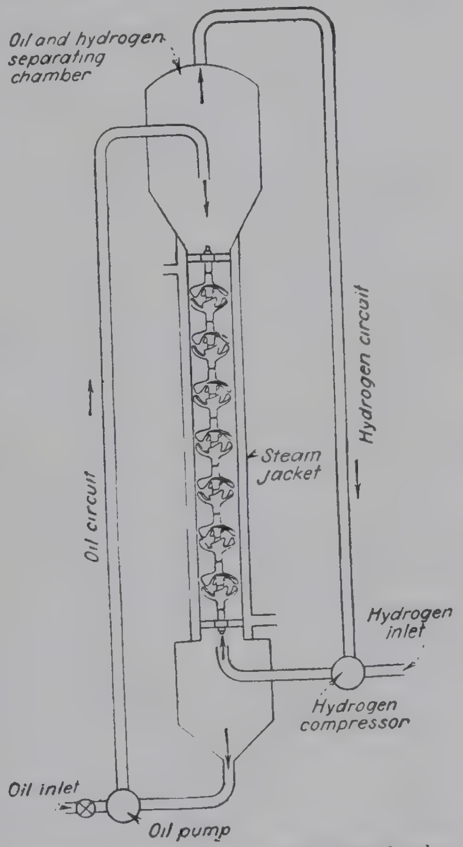

Fig. 6.—Recycling apparatus for hydrogenating oils.

The third type, or continuous process, involves the use of a massive or rigid catalyst over which the hydrogen-oil mixture passes. This procedure obviates the use of filtration for removing the catalyst from the oil and, with respect to its capacity, usually makes the plant more compact. The nickel catalyst is in the form of a wire screen or turnings contained in tubes or reactors. The hydrogen-oil mixture may flow in the same or in countercurrent directions. Generally, more than one reactor is used, and these are provided with suitable connections so that they may be operated in series or in parallel with one another. This permits either the capacity or extent of hydrogenation to be varied readily. The process developed by Bolton and Lush uses a nickel catalyst in the form of turnings or wire, prepared in a special way.[2] In order to get active nickel, the nickel metal is oxidized by means of anodic oxidation;

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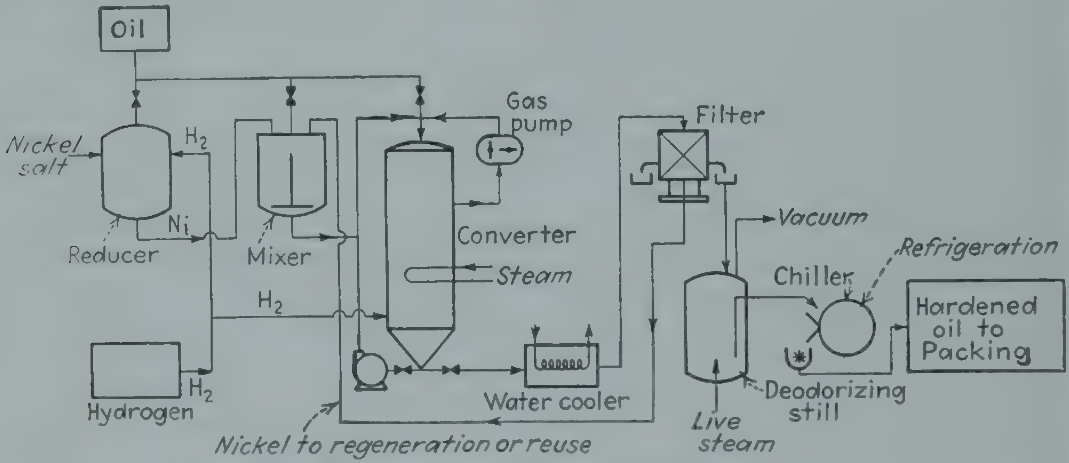
[1] ELLIS, "Hydrogenation of Organic Substances," 3d ed., p. 421, D. Van Nostrand Company, Inc., New York, 1930.

[2] ELLIS, *ibid.*; BOLTON, *J. Soc. Chem. Ind.*, **41**, 384R (1922); **26**, 444T (1927); LUSH, *J. Soc. Chem. Ind.*, **42**, 219T (1912); **43**, 53T (1924); **44**, 129T (1925); **46**, 454T (1927).

i.e., the nickel wires or turnings are made the anode, an electrolyte such as sodium carbonate being used. This does not allow the nickel to pass into solution but converts the surface into nickel oxides, which are then subsequently reduced by hydrogen under carefully controlled conditions. The conditions of operation during hydrogenation are about 180°C. and 60 to 100 lb. per sq. in. hydrogen pressure. The catalyst maintains its activity for relatively long periods of time, but when it needs reactivation the anodic oxidation is again used, the activity of the catalyst being restored on reduction.

In all the various processes for oil hardening, the quantity of nickel used is generally less than 1 per cent by weight of the oil hardened. In those operations where the nickel catalyst needs to be removed from the oil, it is usually done by filtration of the hot liquid fat. The catalyst is then washed, redissolved, and reused in preparing fresh catalyst. Thus, except for small mechanical losses, the catalyst is continually reused.



Requirements per Pound of Hardened Oil

Refined cottonseed oil	0.134 gal.	Cooling water	0.6 gal.
Nickel	0.00075 lb.	Steam	0.5 lb.
Hydrogen	0.75 cu. ft.	Electricity	0.1 kw.-hr.

Direct labor 0.0006 man hr.

FIG. 7.—Flow sheet for the hydrogenation of cottonseed oil.

Figure 7 is a flow diagram for the hydrogenation of cottonseed oil.

The Synthesis of Methanol, Higher Alcohols, and Hydrocarbons.—The synthesis of methanol from carbon monoxide and hydrogen is a reversible reaction. The physical aspects of this problem are many and varied, but the combined application of physical and chemical principles has rapidly developed a variety of syntheses from water gas. The methanol, carbon monoxide, and hydrogen equilibrium has been the subject of several investigations. The following values of the equilibrium constant are available:[1]

$$K_p = \frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}$$

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[1] NEWTON and DODGE, *J. Am. Chem. Soc.*, **56**, 1287–1291 (1934).

TABLE XVIII.—THE EQUILIBRIUM CONSTANT K_p, FOR THE METHANOL SYNTHESIS

Temperature, °C.	K_p
260	1.5×10^{-3}
300	3.1×10^{-4}
340	8.7×10^{-5}
380	2.7×10^{-5}

These data show that the equilibrium constant is small and that it decreases rapidly with temperature. Consequently, the temperature interval over which the synthesis is operative from a practical viewpoint is not very large. At temperatures much below 300°C. (572°F.), the rate of reaction is slow, so that the capacity of the apparatus is small. Above 400°C. (752°F.), the equilibrium becomes too unfavorable. Despite the small values of the equilibrium constant, very satisfactory conversions are obtained. This is because of the decrease in volume attending the reaction

$$CO + 2H_2 \rightleftarrows CH_3OH$$

so that by the application of pressure, the reaction is driven to the right, or to higher conversions. Thus, at 300°C. and 3500 lb. per sq. in., using the theoretical mixture, *i.e.*, one volume of carbon monoxide to two of hydrogen, the equilibrium yield is above 60 per cent, whereas, under exactly the same conditions but working at 150 lb. pressure, the yield is less than 2 per cent. The pressures used in this synthesis are usually from 3,000 to 4,000 lb. per sq. in.

Along with the synthesis of methanol, other side reactions, or parasitic reactions, are possible. Some of these are

$$CO + 3H_2 \rightarrow CH_4 + H_2O + 50{,}000 \text{ cal.}$$
$$2CO + 2H_2 \rightarrow CH_4 + CO_2 + 60{,}280 \text{ cal.}$$
$$2CO \rightarrow C + CO_2 + 41{,}950 \text{ cal.}$$
$$xCO + yH_2 \rightarrow \text{high-molecular-weight alcohols, hydrocarbons, etc.}$$

Not only do these reactions consume carbon monoxide and hydrogen, but they also make control more difficult, for they are more exothermic than the methanol reaction. Such reactions as the last type tend to build up heavy nonvolatile materials, which impair the catalyst's activity. In this synthesis, a catalyst is selected that causes reduction principally to methanol, and a variety of materials are now known to do this surprisingly well, with practically complete exclusion of the side reactions.

The carbon monoxide-hydrogen mixture is usually prepared from water gas, the water-gas catalytic reaction being used to furnish the desired ratio of hydrogen to carbon monoxide. There are, however, instances where carbon dioxide-hydrogen mixtures are available, and methanol is also made readily from these under practically the same conditions as would be used for carbon monoxide-hydrogen mixtures. The reaction

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$$

produces a methanol-water solution instead of pure methanol. Despite the apparent simplicity of the raw materials, a large variety of complex organic products can be readily obtained by only minor changes in the catalyst and operating conditions. This is because condensation as well as hydrogenation reactions occur.

The catalyst is contained in special reactors (Fig. 8) designed to withstand the pressures and temperatures used. By heat interchange either in the reactor or in special heat exchangers, the heat of the reaction—some 24,620 cal. per gram mole of methanol formed—is absorbed. Some of this is used to heat the entering gas to reaction temperature. By proper choice of the space-time yield, or, in other words, the amount of methanol produced per volume of catalyst per hour, and the amount of heat removed in the heat exchangers, the temperature of the catalyst can be kept reasonably constant. Once started, the reaction is self-supporting; *i.e.*, the problem is one of heat removal and not addition.

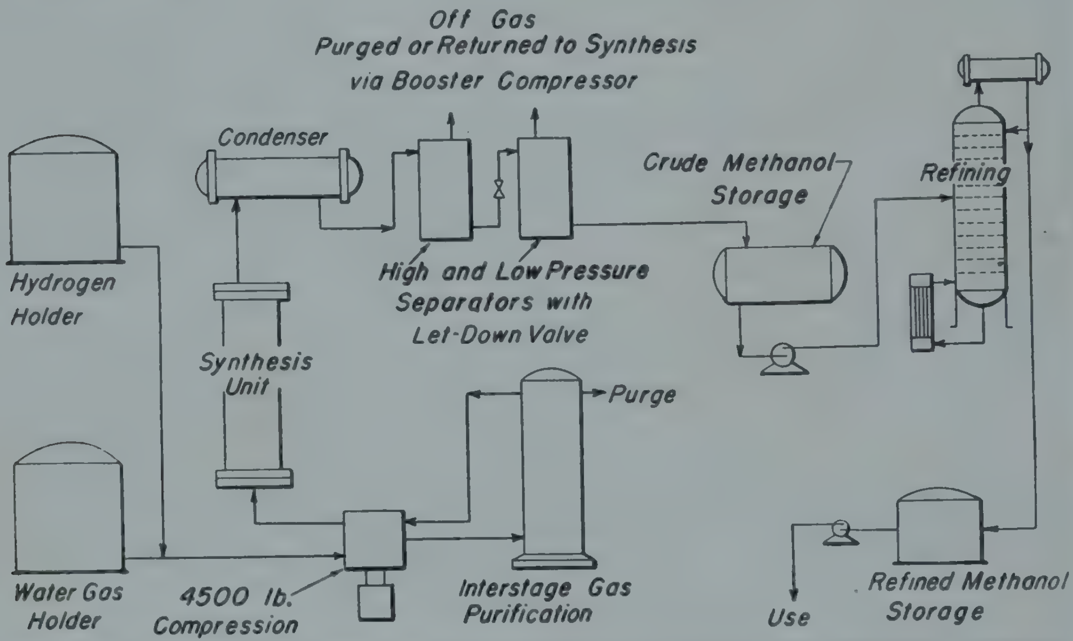

Off Gas
Purged or Returned to Synthesis
via Booster Compressor
Condenser
Crude Methanol
Storage
Refining
Hydrogen
Holder
High and Low Pressure
Separators with
Let-Down Valve
Synthesis
Unit
Purge
Water Gas
Holder
4500 lb.
Compression
Interstage Gas
Purification
Use
Refined Methanol
Storage

FIG. 8.—Flow sheet for the synthesis of methanol from carbon monoxide and hydrogen. (*Ammonia Dept., E. I. duPont de Nemours & Company, Inc.*)

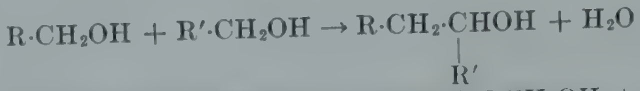
The methanol-containing gases leave the reactor and, after passing through heat exchangers (not shown in Fig. 8), are finally led through condensers where the methanol is condensed, usually under full operating pressures (3,000 to 4,000 lb. per sq. in.). This procedure frees the gas more completely of methanol than if the condensation took place at lower pressure. Any drop in pressure in the reactor and cooling system is repressured by *booster compressors*. If a gas mixture other than the 1:2 ratio of carbon monoxide to hydrogen is used, the composition of the gases must be continually adjusted as it is recycled, and provision must also be made for venting inert or other gaseous side-reaction products. It has been found that the partial pressure of carbon monoxide is the dominant factor upon which the rate of fouling of the catalyst depends owing to adsorption of high-molecular-weight nonvolatile compounds. For this reason, a higher hydrogen-to-carbon monoxide ratio than the theoretical one of 2:1 is sometimes used.

The catalysts usually consist of metal and metallic oxide mixtures, the most common constituents being copper with oxides of zinc, chromium, manganese, and aluminum. For the synthesis of methanol alone, contact of the hot gases with iron should be avoided. In this case, the reactors are lined, usually with copper or some other material not affecting the catalyst. The catalysts for pure methanol are usually susceptible to iron carbonyl, formed when carbon monoxide is in contact with iron. This impairs the catalyst's activity or else induces undesirable side reactions. Practical operations usually involve the production of other alcohols along with methanol. In this case, a somewhat different type of catalyst is used; the presence of iron is not particularly objectionable, since it also catalyzes the formation of higher alcohols from carbon monoxide-hydrogen mixtures.

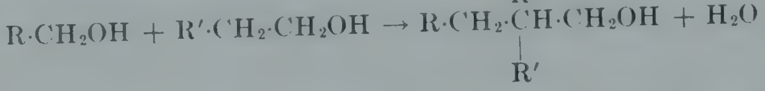
With the proper catalyst and the exclusion of sulfur and iron, methanol of a purity of 99 per cent or better can be produced. As an alternative, methanol may result as part of the synthesis of other valuable higher alcohols, where the exclusion of iron is no longer necessary. The largest single use of methanol is for the preparation of formaldehyde, this product consuming some 45 per cent of the production. Denaturing operations use about 25 per cent of the production; miscellaneous solvents, some 15 per cent; and the manufacture of dimethylaniline, dimethylamine, and methacrylates, about 10 per cent.

Higher alcohols are produced when operating temperatures are slightly higher (350 to 475°C.) than those used in methanol synthesis and with methanol catalysts containing alkalies or else iron-base catalysts containing alkalies. The reaction product may be so complex that complete separation and identification of the constituents are very difficult. Of course, the lower molecular-weight alcohols are more readily separated and identified, and, for this reason, this synthesis has been one of the principal sources of solvents for nitrocellulose and resinous products.

Although the mechanism of the formation of these higher alcohols is not entirely understood and several theories have been suggested, the following method of formation appears the most probable. Certain steps in it have been demonstrated experimentally.[1] This scheme involves three simple assumptions, which are: (1) Higher alcohols result from intermolecular dehydration of two lower alcohol molecules; (2) dehydration involves removal of hydrogen either from the hydroxylated carbon atom, thus producing secondary alcohols (except in the case of methanol), or from the carbon atom adjacent, producing primary alcohols; (3) hydrogen separates most readily from a $>CH_2$ group, with more difficulty from a $—CH_3$ group, and not at all from a $\equiv CH$ group. For example:



$$R\cdot CH_2OH + R'\cdot CH_2OH \rightarrow R\cdot CH_2\cdot \underset{\substack{|\\ R'}}{C}HOH + H_2O$$



$$R\cdot CH_2OH + R'\cdot CH_2\cdot CH_2OH \rightarrow R\cdot CH_2\cdot \underset{\substack{|\\ R'}}{C}H\cdot CH_2OH + H_2O$$

The higher alcohol mixture has been found to contain the following primary alcohols: *n*-propanol, isobutanol, 2-methyl-1-butanol, 2-methyl-1-pentanol, 2,4-dimethyl-1-pentanol, 4-methyl-1-hexanol; and the following secondary alcohols: isopropanol, 3-methyl-2-butanol, and 2, 4-dimethyl-3-pentanol. In addition, there are definite indications of 2, 4-dimethyl-1-hexanol, 4 or 5-methyl-1-heptanol, 3-pentanol, 2-pentanol, and 2-methyl-3-pentanol.[2]

The Synthesis of Liquid Hydrocarbon by the Reduction of Carbon Monoxide.—When carbon monoxide-hydrogen mixtures are passed over cobalt, iron, nickel, and some copper catalysts that are promoted with certain metallic oxides, particularly oxides of the alkali metals, at temperatures in the range from about 200 to 300°C. and pressures from about 1 to 25 atmos., various hydrocarbons are formed according to the following type reactions:

$$x\text{CO} + \left(x + \frac{y}{2}\right) \text{H}_2 = \text{C}_x\text{H}_y + x\text{H}_2\text{O}$$

$$2x\text{CO} + \left(\frac{y}{2}\right) \text{H}_2 = \text{C}_x\text{H}_y + x\text{CO}_2$$

These hydrocarbons may contain from 1 to 50 or more carbon atoms in varying degrees of saturation with hydrogen. They may comprise chain or ring systems that are saturated or unsaturated. These reactions, known as the Fischer-Tropsch synthesis of hydrocarbons, are important and have great potentialities. It is estimated that nearly a million tons of fuel were produced annually in Germany in 1940 to 1943 by this method. This procedure enables coals, coke, tars, and refinery and natural gas to be converted into gasoline, Diesel fuel, and wax as the main products. The olefinic products can be polymerized to synthetic lubricating oils or utilized by the OXO process to make alcohols, or the paraffinic materials can be oxidized to produce fats and detergents. The fuels can have a wide range of octane or cetane numbers.

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[1] GRAVES, *Ind. Eng. Chem.*, **23**, 1381 (1931); FROLICH and CRYDER, *Ind. Eng. Chem.*, **22**, 1057 (1930).

[2] GRAVES, *ibid.* (1931).

Modifications of this process will be used in this country to convert natural gas, coal, and lignite into liquid fuels. At present, the large reserves of natural gas are a better starting material and can be processed more easily than coal. Table XIX shows how coal and methane compare as materials for making gasoline by the Fischer process.

TABLE XIX.—EFFICIENCIES OF GASOLINE PRODUCTION BY FISCHER-TROPSCH PROCESS[1]

Raw material	Raw material needed to produce 1 bbl. of gasoline, lb.	% of fuel value of raw material converted to gasoline
Coal	1,306	31
Methane	440–505	42–48

[1] OBERFELL, *Oil Gas J.*, **44**, No. 32, 77 (1945).

A suitable synthesis gas can easily be prepared from either material (pages 492–494).

The principal variables affecting these reactions are as follows: the type of catalyst, the temperature and pressure, the ratio of carbon monoxide to hydrogen, the contact time, the purity of the synthesis gas, and the means for controlling the reaction temperature within fairly narrow but definite limits.

Cobalt catalysts have been used extensively in Germany for this synthesis. A common catalyst consists of cobalt, thoria, and kieselguhr in the weight proportions of 100:18:100. The temperatures are usually around 200°C. and the pressures less than 5 atmos. in commercial operation. The products are usually of the paraffinic type. During operation, high-molecular-weight waxes build up on the cobalt catalyst, and these waxes must be removed to maintain the catalyst's activity. This can be done by washing the catalyst with hot hydrocarbon solvents. Pressure affects the type of products formed, as shown by the data in Table XX. With cobalt catalysts, the yields range from about 120 to 170 ml. of liquid per cubic meter of synthesis gas. The maximum theoretical yield is about 208 ml. of liquid per cubic meter of gas containing carbon monoxide and hydrogen in the molal ratio of 1:2.

Iron catalysts promoted with copper and alkali have also been used for this synthesis. In this case, the temperatures are usually around 250 to 300°C. and the pressures are higher than for cobalt-type catalysts. The liquid products are usually more unsaturated and contain considerable olefins. The olefin content can be further increased by increasing the carbon monoxide content of the synthesis gas. The tendency to build up high-molecular-weight waxes is less than with cobalt catalysts. Obviously, iron is a more economical and available catalyst. As the copper content is increased, more oxygenated products are usually formed.

TABLE XX.—THE EFFECT OF PRESSURE ON THE PRODUCTS OBTAINED USING A COBALT-TYPE CATALYST[1]

Pressure, atmos.	Yield, gm. per cu. m. of synthesis gas				
	Total yield of solid and liquid products	Paraffin wax	Oil boiling above 200°C.	Gasoline boiling below 200°C.	Gaseous hydrocarbons, including C_3 and C_4
1.0	117	10	38	69	38
2.5	131	15	43	73	50
6.0	150	60	51	39	33
16.0	145	70	36	39	33
51	138	54	37	47	21
151	104	27	34	43	31

[1] LOWRY, *loc. cit.*, p. 1826.

Nickel is not well suited for these syntheses, for the tendency to form methane is too great. If pressure is applied to alter the reaction, nickel carbonyl is formed which is volatile. At best, nickel appears to find limited use as a promoter.

Along with hydrocarbons, there are usually formed small amounts of oxygenated products, such as alcohols and ketones. These can be separated, and they offer interesting possibilities of producing organic chemicals together with the synthesis of gasoline and other fuels.

The synthesis gas must be free of sulfur, for it readily poisons these catalysts. It would be highly desirable to have sulfur-resistant catalysts for these hydrocarbon syntheses.

The synthesis reactions liberate considerable heat which must be removed. Otherwise, the catalyst temperatures will reach values where wasteful side reactions predominate or where the catalyst's activity is seriously jeopardized.

The method by which this reaction heat is removed is important in determining the operability of the process. Cooling devices have been used in which water under pressure is circulated through the catalyst bed.[1]

Hydrogenation of Acids or Esters to Alcohols.—The direct reduction of the carboxyl group to an alcohol by means of molecular hydrogen and catalysts occurs at temperatures usually from 300 to 400°C. (570 to 750°F.) and with hydrogen pressures of about 3,000 lb. per sq. in. The acids or esters may be of the long, straight-chain type such as occur in vegetable oils and fats, or they may be of the shorter chain type, with more complicated groupings or branchings. The oil-hardening processes use long-chain acids and esters and saturate only the olefinic linkages in the carbon chain; in the reductions to be described here, the carboxyl group (—COOH) is changed to an alcohol group (—CH_2OH), and the olefinic bonds in the chain may or may not be reduced at the same time. This is again an illustration of the remarkable specificity of catalysts; normally, the olefinic bonds would be considered far more reactive in hydrogenations than a carboxyl group. Yet they may not be reduced while the carboxyl group is being converted to an alcohol.

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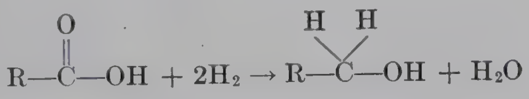
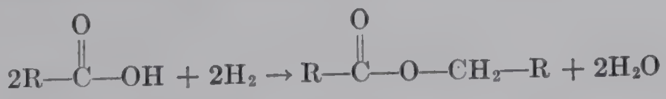
[1] LOWRY, "Chemistry of Coal Utilization," Vol. II, p. 1819, John Wiley & Sons, Inc., New York, 1945.

The earlier methods of reducing acids or esters to alcohols involved the use of metallic sodium with anhydrous alcohols; also, an acid derivative, such as the acid chloride, could be reduced by direct hydrogenation to an aldehyde by palladium catalysts. The direct reduction, using molecular hydrogen at high pressure, involves 2 moles of hydrogen per mole of acid reduced, as shown in the following reaction:



$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH + 2H_2 \rightarrow R\text{—}\overset{H\;\;H}{C}\text{—}OH + H_2O$$

where R represents a group preferably of the aliphatic or the hydroaromatic series. A secondary reaction consists of esterfication of a portion of the alcohol formed with a portion of the unchanged acid. The proportion of ester present in the product depends chiefly on the completeness of the hydrogenation. When the reaction is conducted under conditions that yield only partial reduction of the acid, the process may be altered to give esters as the main products, according to the equation:



$$2R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH + 2H_2 \rightarrow R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}CH_2\text{—}R + 2H_2O$$

If R in these formulas contains an unsaturated or olefinic bond, partial reduction of the carbon-carbon unsaturation may occur. It is sometimes more suitable to conduct the reaction to favor alcohol or ester formation and then further reduce the olefinic bonds at lower pressures and temperatures with nickel catalysts in the same manner as that used in hardening oils. This brings all the reaction products to the same completeness of hydrogenation, yielding new compositions—usually solids—from which alcohols and esters may be separated if desired. The stability of high-molecular-weight acids and alcohols under high-pressure hydrogen at high temperatures is very different from that which would be expected when heating these compounds in air. Decarboxylation of the acid to form carbon dioxide and a hydrocarbon of fewer carbon atoms does not occur in hydrogenation. The dehydration of the alcohol to an olefin, or the more complete reduction of the —CH_2OH to a —CH_3 group, occurs only slightly. However, this is dependent on the other groups near the alcohol group; with straight hydrocarbon chains, these decompositions occur to a very minor extent.

The reductions may be carried out in a batch system or in a flow system, the latter being preferable. The catalyst in granular form is held in place in a heated tube capable of withstanding the pressure and temperature. The acid or ester, if solid, may be melted or may be dissolved in a solvent such as normal butyl alcohol or ethyl alcohol, and it is then pumped into the reactor and over the catalyst. The use of acids or esters of the acids and simple alcohols is preferable to the use of the glycerides, because the presence of glycerol and its decomposition products makes the separation of the reaction products difficult. The acid or ester is pumped through the reactor at the rate of 2 to 8 volumes of material per volume of catalyst per hour, a considerable excess of hydrogen being passed along with the material over the catalyst. From 2 to 10 moles of hydrogen is used per mole of acid hydrogenated.[1] The proportion of esters to alcohols produced in the hydrogenation will depend on the ratio of hydrogen to the acid being reduced.

The catalysts are of the mild hydrogenating type, such as supported copper, copper chromite, zinc-copper chromate, nickel-copper zincate, and sometimes certain salts of molybdic acid. These catalysts usually require a reduction with hydrogen prior to use. A specific catalyst preparations is as follows: A solution is prepared by dissolving 245 parts by weight of crystallized zinc nitrate, 23 parts of hydrate cadmium nitrate, and 24 parts of copper nitrate in about 750 parts of water. A second solution is prepared by dissolving 100 parts by weight of chromic anhydride (CrO_3) in 500 parts of water and then adding 135 parts of 28 per cent aqueous ammonia. Precipitation of the hydrogenating metals of the first solution as chromates is effected by stirring and adding the second solution at room temperature. The mixture is exactly neutralized with additional ammonium hydroxide and allowed to settle. The clear supernatant liquid is poured off, and the precipitate is washed several times by decantation with an adequate volume of wash water, after which it is filtered and dried at about 100°C. The next step consists of igniting the dried filter cake at 400°C. for 4 hr. This process converts the double ammonium chromates of the copper, zinc, and cadmium to metallic chromites, in which form they are employed as catalyst. Suitable physical form is obtained by granulating the friable chromite powder and briquetting it into the form of tablets, which may or may not be broken up into grains of various sizes. In some cases, it is advisable to prereduce the hydrogenation catalyst with hydrogen or other reducing gas before loading it into the converter. In others, the catalyst reduction is carried out *in situ* by heating up slowly in a stream of hydrogen, prior to the introduction of the acid to be hydrogenated.[1]

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[1] Lazier, U. S. 1,839,974 (1932).

Coconut oil is one of the vegetable oils commonly hydrogenated to produce alcohols. In this case, the alcohols comprise octyl, decyl, lauryl, myristyl, cetyl, and stearyl. They are valuable chemicals used in the manufacture of detergents, petroleum additives, solvents, and plasticizers.

Hydrogenation of Hydrocarbons, Petroleum, Tar, and Coal.—The purposes of hydrogenating hydrocarbons, petroleums, tars, and coals are (1) to improve existing petroleum products or develop new uses and products; (2) to convert inferior or low-grade materials such as heavy oils and tars into valuable petroleum products; and (3) to transform solid fuels such as lignites and coals into liquid fuels. The distinguishing feature of these operations is that both the raw materials and finished products are very complex mixtures of relatively unknown composition. All types and sizes of molecules are present along with a variety of contaminating impurities. Thus, in the hydrogenation process, a variety of reactions may be occuring simultaneously and to varying extents, and yet the final product may be very satisfactory, meeting all the required specifications.

These complicated mixtures are identified and recognized by certain properties, sometimes more physical than chemical in character. Thus, gasoline specifications are concerned with sulfur content, gum-forming materials, general stability and resistance to chemical change or oxidation, and detonation and volatility characteristics. Kerosenes are identified by their sulfur content, specific gravity, burning qualities, and volatility. Lubricating oils are judged by their stability toward heat and oxidation, their carbon-forming tendencies, lubricating qualities, viscosity characteristics, color, and volatility. Tars are recognized by their aromatic and phenolic hydrocarbon content, their specific gravity, volatility, and viscosity. Coals are classified according to their age; ash content; the carbon, hydrogen, nitrogen, oxygen and sulfur analysis; and the volatile matter. Hydrogenation may result in an upgrading of one or all of the properties of the material. In processing petroleums, tars, and coals, the operation is far more complex than in working with pure or relatively pure materials.

Catalysts not only must speed up these hydrogenations but also must guide and direct the desired reactions and effect a balancing and harmonizing of many factors so that just the correct over-all result is attained. They must also be able to operate on liquid, solid, or gaseous materials and, in addition, cause impurities that are common catalytic poisons, such as sulfur, oxygen, and nitrogen, to be detached from their molecular linkages and removed as hydrogen sulfide, water, or ammonia. All these things the hydrogenation catalysts must do rapidly and at relatively low temperatures. Although at first it may seem incredible, catalysts are now known that perform all these functions satisfactorily. The elements of group 6 of the Periodic System are very suitable, particularly molybdenum, tungsten, and chromium, as oxides or sulfides or more complicated mixtures with one another.

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[1] **Lazier**, U. S. 1,839,974 (1932).

The extent to which these new catalysts increase the velocity of hydrogenation is indicated in the case of effecting improvements in lubricating oils.[1] At 200 atmos. pressure, there was no improvement without catalysts; and even at 1,000 atmos. without catalysts, the improvement, if any, was very slight. The hydrogenation velocity in the presence of catalysts and about 200 atmos. pressure is, however, about a hundred times greater than without catalysts. In the conversion of heavy, nonvolatile materials into lighter products such as gasoline, the catalyst must favor cracking reactions as well as hydrogenation reactions. Yet these two must be in the proper balance. Cracking must not proceed faster than the hydrogenation of the cracked products; condensation and polymerization of unsaturated or reactive molecular fragments must not proceed faster than their hydrogenation. Otherwise, high-molecular-weight products would accumulate on the surface of the catalyst, decreasing or completely destroying its activity. With the conditions of temperature, pressure, and catalyst delicately coordinated, complex hydrogenations proceed with surprising smoothness.

TABLE XXI.—EXOTHERMIC HEAT OF REACTION OF DIFFERENT HYDROGENATION REACTIONS

Reaction	Raw material	
	Cal. per gm.	B.t.u. per lb.
Hexane + H_2 → methane	730	1315
Bituminous coal + H_2 → light oil	450	810
Middle oil from bituminous coal + H_2 → gasoline	400	720
High boiling crude oil fraction + H_2 → lubricating oil	50	90
N_2 + H_2 → ammonia	750	1350
CO + H_2 → methanol	700	1260

Hydrogenations involving petroleum, tar, or coal are usually exothermic. Table XXI sets forth some of the approximate quantities of heat liberated by different hydrogenations.[2]

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[1] GRIMM, *Intern. Conf. Bituminous Coal*, **II**, 49 (1931).

[2] *Ibid.*, p. 477.

The hydrogen consumed in the process obviously depends on the difference in hydrogen content of the raw material and finished product and on the extent to which gases containing methane and other low-boiling hydrocarbons are formed. In the hydrogenation of bituminous coals and tars derived from such coals, from 8 to 16 cu. ft. of hydrogen is required per pound of coal. In crude oils, poor in hydrogen, the consumption is about 3 to 6 cu. ft. of hydrogen per pound of oil, but in oils rich in hydrogen, from 0.5 to 2 cu. ft. per lb. is consumed. These data are for reductions in which no gaseous products form.

The additional hydrogen consumption for gasification depends on the extent of the hydrogenation, whether paraffinic or aromatic products are formed, and the hydrogen content of the raw materials. In processing coal or coal tars, the hydrogen consumed in making gaseous products such as methane and its homologues is about 0.3 to 0.4 cu. ft. per lb. of charging stock for each 1 per cent of gaseous products; in processing petroleum, brown-coal tars, and the light oils, the gaseous products use about 0.15 to 0.25 cu. ft. of hydrogen per pound of material charged.

The yield of liquid reaction products will depend on the amount of gasification during hydrogenation. A yield of 55 per cent by weight or more of marketable gasoline appears possible by hydrogenating brown coals or lignites. With suitable bituminous coals, it may be 65 per cent by weight or more. These figures are for the ash-free dry coal. In the case of tars, the yield may be 80 to 85 per cent by weight, which is over 100 per cent yield by volume.

In operating hydrogenation processes, it has been found advantageous to divide them into two parts: (1) liquid-phase reactions, where pulverized coal and *pasting* oil or heavy oils are contacted with hydrogen, and (2) gas-phase reactions, where the light oil exists practically entirely in the gas phase during hydrogenation. It has been found, in processing heavy oils or in processing coals in one step, that the extent of hydrogenation was insufficient and the yield low because heavy materials tended to be preferentially adsorbed, thus excluding the light oils from hydrogenation. Under these conditions, the latter accumulate; and instead of being hydrogenated to gasoline, uncontrolled cracking and polymerization reactions take place. The polymerization of unstable materials produced by cracking builds up high-molecular-weight compounds, resulting in low yields of gasoline. These difficulties are avoided in the two-step operation for producing gasoline. Materials with normal boiling points below about 300 to 350°C. (570 to 660°F.) are used in the gas-phase operation: those boiling higher than this are hydrogenated in the liquid phase.

Petroleum Hydrogenation.—The principal uses of petroleum hydrogenation in this country are as follows:[1]

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[1] HASLAM and RUSSELL, *Ind. Eng. Chem.*, **22**, 1030 (1930); SWEENEY and VOOR-

Production of a high-octane-number saturated type of aviation gasoline from olefinic naphthas and gasolines.

Production of special high-octane blending fuels for aviation gasoline by saturating branched-chain olefins produced by polymerization. Hydrocodimer manufacture is typical of this operation.

Production of safety fuels of high flash point and high octane number.

Production of water-white paraffinic kerosenes from inferior-quality distillates.

Production of high-grade paraffinic Diesel fuels from low-quality gas oils.

Production of naphthas or solvents of low aniline point and high solvency and flash point.

Improvement in lubricating-oil quality and the production of high-viscosity-index lubricants from poor-quality lubricating distillates.

Conversion of asphaltic crudes and refinery residues into paraffinic and low-boiling gas oils or into high-quality motor gasoline.

Upgrading of catalytic and thermal cycle stocks to produce high-quality gas oils and gasolines.

In the first four operations listed above, the principal reaction is the addition of hydrogen to unsaturated or olefinic linkages without causing a marked cleavage of carbon-carbon bonds. It is generally desired to avoid extensive hydrogenolysis in these processes. When the materials are free of sulfur, nickel-type catalysts are frequently used. Otherwise, metal sulfide or oxide types that are sulfur resistant have to be employed. Since these reactions are essentially simple types of hydrogenation and do not involve primarily molecular cleavage, the temperatures and pressures employed are relatively low. The temperatures are usually in the range of 200 to 350°C., and the hydrogen pressures may range from about 10 to 50 atmos.

Figure 9 shows a flow sheet for the hydrogenation of olefinic hydrocarbons to produce high-octane fuel components for aviation use.[1] In this case, the feed may be a mixture of seven- and eight-carbon atom branched-chain olefins. These are converted to the corresponding saturated or paraffinic hydrocarbons, which are valuable blending agents for making high-octane-number aviation fuel. The hydrogenation may be accomplished in one or two stages. Where the cost of the hydrogen is relatively high and it is desired to make the most effective use of it, two-stage hydrogenations are employed; in this way, about 95 per cent of the hydrogen may be utilized.

HIES, *Ind. Eng. Chem.*, **26**, 195 (1934); MURPHREE, BROWN, and GOHR, *Ind. Eng. Chem.*, **32**, 1203 (1940); BROWN, VOORHIES, and SMITH, paper before Division of Petroleum Chemistry, Am. Chem. Soc., September, 1945.

[1] *Heat Engineering*, **14**, 71, May, 1939, issued by Foster Wheeler Corp., New York

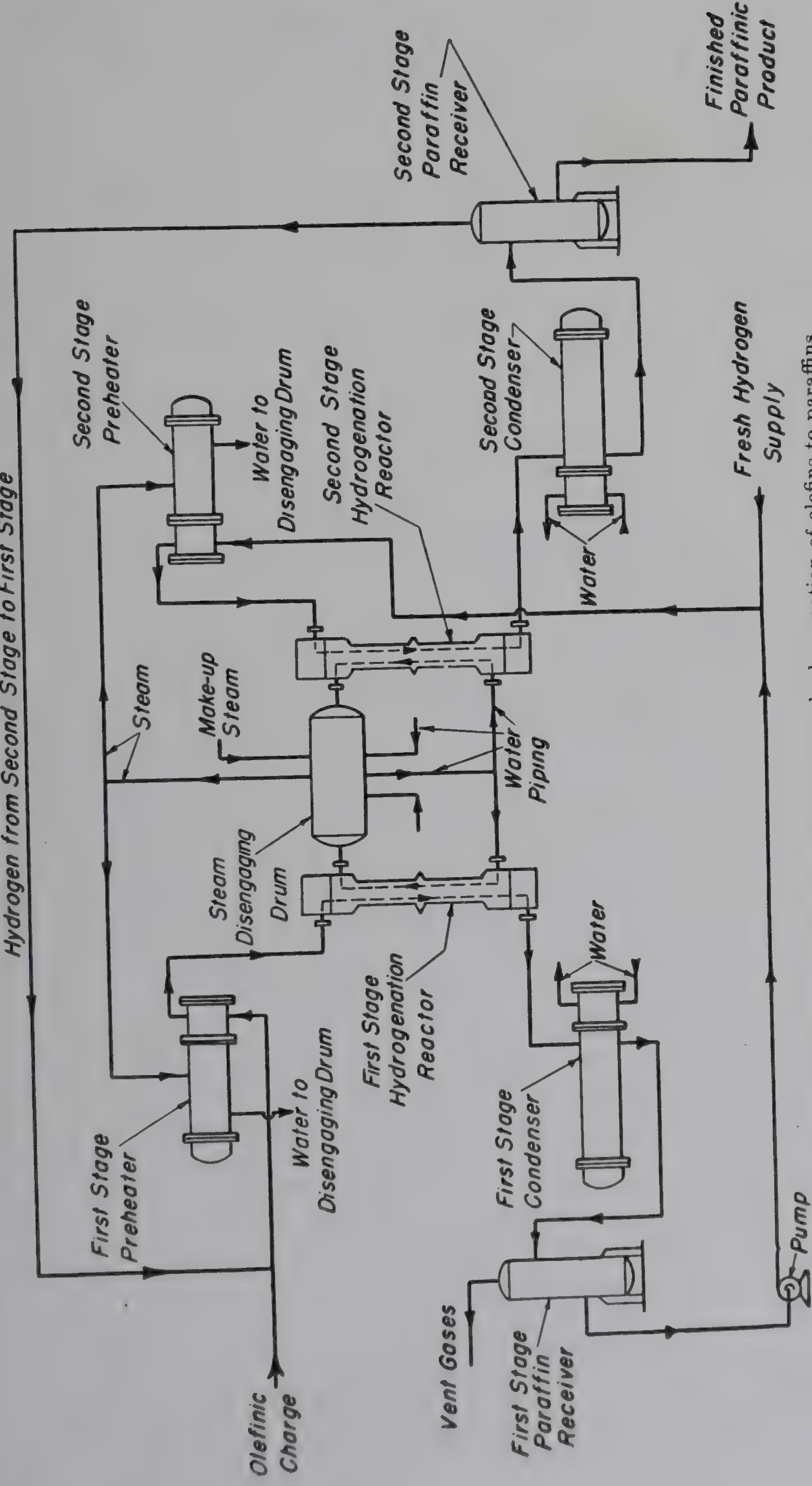
Hydrogen from Second Stage to First Stage
Second Stage Preheater
Water to Disengaging Drum
Second Stage Hydrogenation Reactor
Second Stage Condenser
Second Stage Paraffin Receiver
Finished Paraffinic Product
Fresh Hydrogen Supply
Water
Steam
Make-up Steam
Water Piping
Steam Disengaging Drum
First Stage Hydrogenation Reactor
First Stage Condenser
First Stage Preheater
Water to Disengaging Drum
Water
Olefinic Charge
Vent Gases
First Stage Paraffin Receiver
Pump

FIG. 9.—Flow sheet for the low-pressure hydrogenation of olefins to paraffins.

The olefinic charge is combined with unreacted hydrogen from the second stage, and both are passed through a steam-heated preheater and then into the top of the first stage hydrogenation reactor. Here the olefin-hydrogen mixture intimately contacts the catalyst which induces saturation of the olefinic linkage.

The reactor consists of a steel shell containing a multiplicity of tubes filled with catalyst. Since this hydrogenation reaction is exothermic, water is maintained in the shell of the reactor and in the space around the catalyst tubes to limit the reaction temperature and to pick up the heat of the reaction. This is accomplished by allowing the water to vaporize under pressure to generate steam. This high-pressure steam is then used in the preheaters to heat the incoming olefin-hydrogen mixture.

The vaporized olefins are partially hydrogenated as they flow downward through the first-stage reactor. They are withdrawn at the bottom of the reactor, condensed in a conventional type of shell-and-tube condenser, and collected in the first-stage paraffin receiver. Noncondensable gases, resulting from side reactions, are vented from the receiver into the atmosphere.

A pump draws the partially hydrogenated product from the first-stage receiver and feeds it to the second-stage preheater. At this point, a fresh supply of hydrogen is introduced into the hydrocarbon stream, and the mixture is preheated as before in the second-stage preheater. From here, the mixture flows downward through the catalyst in the tubes of the second-stage reactor. As in the first stage, water in the shell of the reactor removes the heat liberated during the hydrogenation, and the resulting steam is used to provide the proper preheating.

The paraffin hydrocarbons and excess hydrogen pass from the bottom of the reactor through a condenser where the hydrocarbons condense. In the second-stage paraffin receiver, the hydrogen is separated for return to the first-stage reactor, while the fully hydrogenated paraffinic product is sent to storage, thereby completing the operation.

In the conversion of asphaltic residua or in the upgrading of highly aromatic or refractory cycle stocks or gas oils, cracking or pyrolysis occurs along with the hydrogenation reaction. These materials contain varying proportions of highly condensed aromatic structures of the naphthalene, phenanthrene, pyrene, etc., types, and, when they are cracked in the absence of hydrogen, tars and coke commonly result.

If high-molecular-weight petroleum fractions are simply pyrolyzed, *i.e.*, no hydrogenation occurs, then progressive cracking and polymerization generally lead to the final products: (1) gaseous and low-boiling liquid compounds of high hydrogen content; (2) liquid material of intermediate molecular weight and a hydrogen-to-carbon ratio differing more or less from that of the original feed stock, depending on the method of operation; and (3) liquid material of high molecular weight, such as tar and petroleum coke, possessing a lower ratio of hydrogen to carbon than the starting material.

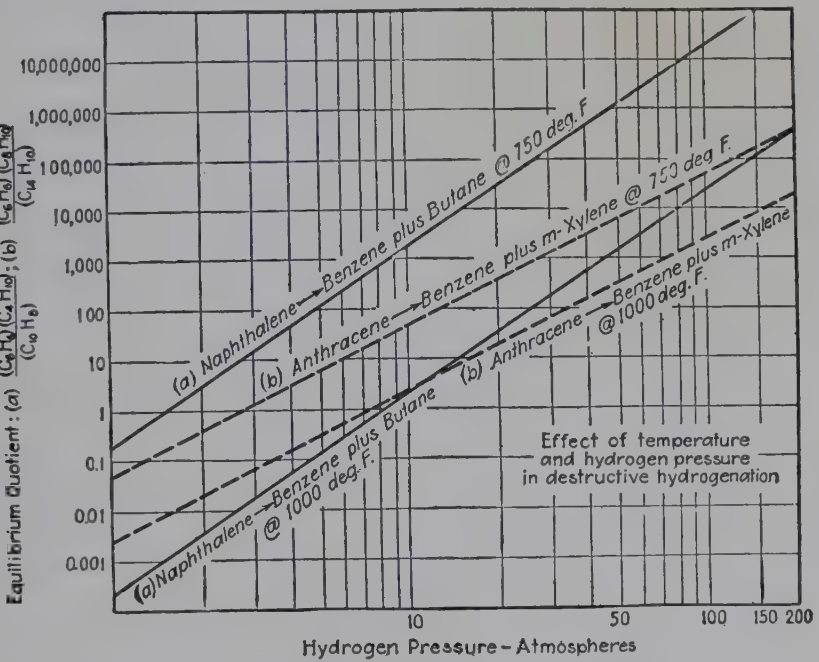

Fig. 10A.—Effect of temperature and pressure on the hydrogenation-dehydrogenation equilibriums.

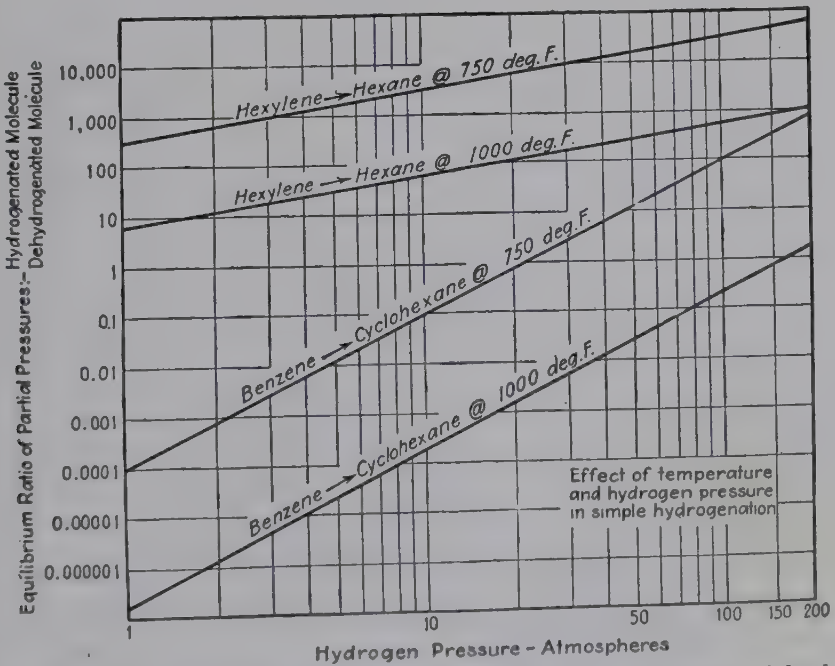

Fig. 10B.—Effect of temperature and pressure on the hydrogenation-dehydrogenation equilibriums.

An essential difference between pyrolysis and hydrogenolysis of petroleum is that in pyrolysis a certain amount of polymerized heavier products, such as tar and coke, is always formed along with the light products, such as gas and gasoline; whereas, in hydrogenolysis or destructive hydrogenation, polymerization may be partly or even entirely prevented, so that only light products are made. The prevention of tar and coke formation usually results in an increased gasoline yield. The condensed type of molecule, such as naphthalene or anthracene, is one that is closely associated with the building up of tar and coke, but, in an atmosphere of hydrogen and in contact with catalysts, these condensed molecules are changed over into lower molecular-weight compounds which are more saturated and boil within the gasoline range. Figure 10 shows the pronounced effect of temperature and hydrogen partial pressure on the hydrogenation-dehydrogenation equilibriums of a few condensed types of hydrocarbons.[1] These data show that it is possible to get varying degrees of hydrogenation. At low temperatures and high hydrogen pressures (200 atmos.), the product can be made very saturated; or if the temperature is raised and the partial pressure of hydrogen lowered, a more aromatic product can be made. These factors are important in producing motor fuels of varying antiknock qualities. The aromatic content, which is related to the antiknock properties of a fuel, can be retained under conditions wherein sulfur compounds and resinous and asphaltic materials are hydrogenated and thus removed or converted into more valuable products.

Table XXII gives some experimental results on hydrogenating gas oil with various catalysts. The gas oil used had a density at 20°C. of 0.894, 73.4 per cent by weight distilling over between 234 to 280°C. and 22.2 per cent between 280 to 310°C.[2] It is evident that molybdenum and tungsten sulfides are effective catalysts for converting gas oil into lower molecular-weight and more saturated products. Such catalysts are not poisoned by sulfur compounds in the oils.

Figure 11 is a flow sheet of the hydrogenation of a heavy gas oil. The oil to be hydrogenated is fed to the system by high-pressure pumps. It is mixed with fresh hydrogen that has been separately compressed to the desired operating pressure, which is usually in the range of 100 to 250 atmos. Additional hydrogen is added in the form of recycle gas which has been separated from the liquid hydrogenated product. This hydrogen is recycled by a booster compressor which essentially makes up the pressure drop through the system. The incoming oil is brought to reaction temperature, usually in the range of about 400 to 540°C., by specially designed heat exchangers and by heating in a direct-fired high-pressure coil or heater. The hydrogenation takes place in high-pressure reaction chambers containing the catalyst. There is a net evolution of

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[1] Sweeney and Voorhies, *loc. cit.*

[2] Tropsch, *Intern. Conf. Bituminous Coal*, **II**, 35 (1931).

TABLE XXII.—HYDROGENATION OF GAS OIL

Temperature, 440°C. (825°F.); Time, 1 Hr.

Catalyst	H_2 pressure, lb. per sq. in.			Yields of reaction products, weight % of gas oil used				Fraction up to 230°C., weight %				Fraction 230 to 270°C., weight %				Liquid reaction products, weight %	
	Initial at 20°C.	Maximum	Final at 20°C.	Gaseous hydrocarbons, %	Liquid hydrocarbons		Loss	Gas oil used	Liquid reaction products	D^{20}_{4}, °C.	Iodine No.	Gas oil used	Liquid reaction products	D^{20}_{4}, °C.	Iodine No.	Residue above 270°C.	Gas + loss
					%	D^{20}_{4}											
No catalyst	1,160	2,800	1,100	3.2	92.4	0.8691	4.4	21.1	22.9	0.800	86.8	40.2	43.5	0.893	39.7	32.1	1.5
MoO_3	1,160	2,800	990	3.3	91.3	0.8675	5.4	20.6	22.6	0.796	42.7	41.7	45.7	0.895	....	30.2	1.5
MoO_3 (reduced by H_2 at 600°C.)	1,160	2,900	1,070	3.6	88.4	0.8650	8.0	22.8	25.8	0.795	....	39.4	44.6	0.897	....	27.8	1.8
MoS_3	1,150	2,600	870	5.5	89.2	0.8324	5.3	43.9	49.3	0.791	20.9	30.0	33.7	0.890	25.3	14.5	2.5
$(NH_4)_2MoS_4$	1,160	2,800	880	4.5	86.8	0.8128	8.7	55.3	64.0	.....	....	22.5	26.0	.....	....	6.4	3.6
$(NH_4)_2MoS_4$ (reduced by H_2 at 500°C.)	1,150	2,600	960	2.9	91.2	0.8523	5.9	32.9	36.2	0.801	....	35.5	39.0	0.886	....	22.9	1.9
Molybdenite (MoS_2)	1,150	2,800	1,050	4.9	88.4	0.8641	6.7	27.0	30.7	0.793	....	38.2	43.4	0.899	....	24.9	1.0
$MoSe_3$	1,160	2,800	1,020	4.6	92.5	0.8520	2.9	32.4	35.0	0.798	....	41.3	44.7	0.892	....	23.3	
WS_3	1,160	2,700	820	5.3	82.7	0.8098	12.0	44.4	54.1	0.765	21.9	24.4	29.7	0.883	....	15.8	0.4
NiS	1,160	3,200	1,020	4.9	93.4	0.8482	1.7	38.0	40.8	0.800	57.1	34.1	36.6	0.893	....	20.5	2.1
ZnS	1,160	2,900	1,050	1.8	90.6	0.8611	7.6	26.4	29.4	0.795	....	37.5	41.8	0.834	....	27.0	1.8

heat, for the reaction is exothermic. To control the temperature, intermediate cooling is sometimes effected by adding cold recycle gas at suitable points in the reactors. After exchanging its heat with the entering mixture of oil and hydrogen, the reaction product passes through a cooler to a high-pressure gas separator where the recycle gas, consisting mainly of hydrogen, is removed. In a low-pressure system following the separator, the products are fractionally distilled as desired to make gasoline, kerosene, etc. The catalysts employed in the reaction chambers are very stable physically and chemically and are not harmed by the normal constituents of petroleum oils, including sulfur compounds. The life of these catalysts may extend to a year or more.

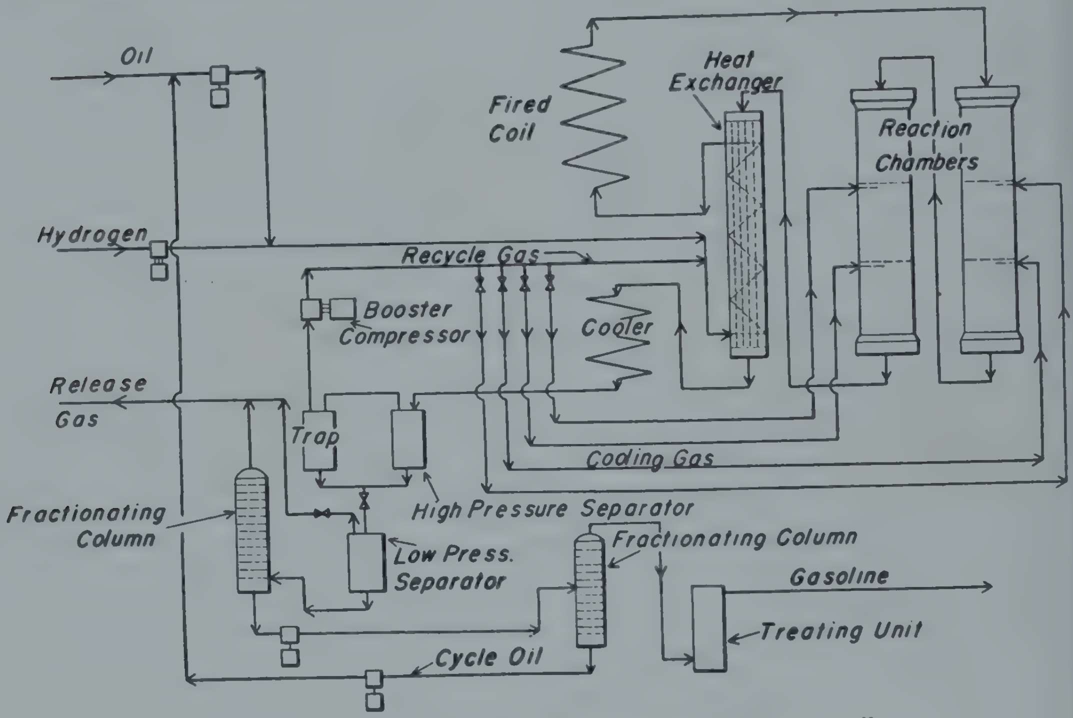
Oil
Hydrogen
Fired Coil
Heat Exchanger
Reaction Chambers
Recycle Gas
Booster Compressor
Cooler
Release Gas
Trap
Cooling Gas
Fractionating Column
High Pressure Separator
Fractionating Column
Low Press. Separator
Gasoline
Treating Unit
Cycle Oil

FIG. 11.—Flow chart for the hydrogenation of heavy oil.

Tar Hydrogenation.—The manufactured-gas and coke-oven industries produce large quantities of tars, and these can be hydrogenated to produce satisfactory motor or Diesel fuels. In Europe, coals are subjected to low-temperature carbonization where the tar yield is considerable, and these tars are then hydrogenated to produce fuels instead of directly hydrogenating the coal. The processing of tar is much easier than that of coal, and the operation is more closely related to petroleum hydrogenation than coal hydrogenation. Practically twice as much motor fuel can be produced by hydrogenating the tars than by cracking them to produce similar products. Molybdenum oxide has been found to be a suitable catalyst, and an even greater activity is shown by molybdenum sulfide. Temperatures of from 450 to 500°C. (840 to 930°F.) are used, and the pressures are approximately 250 atmos. In addition to the catalysts effecting cleavages of hydrocarbons of high molecular weight and hydrogenating these into stable, more volatile products, they must also be able to effect the reduction of phenolic and organic nitrogen compounds to hydrocarbons.

Coal Hydrogenation.—The hydrogenation of coal is a special application of the liquid-phase process. Coal is a complex mixture of very high-molecular-weight compounds, and the successful hydrogenation of it to give high yields of liquid motor fuels depends not only on high-pressure hydrogen but also to a very great extent upon catalysts that facilitate and accelerate the entry of hydrogen into coal or its decomposition products.

In general, the coal is first mixed with a high-boiling oil, called a *pasting oil*, and this mixture is forced into the high-pressure reaction chamber. The coal paste, which is made up of about equal parts of finely ground bituminous or brown coal and a high-boiling oil, is mixed also with a finely divided catalyst, and this highly viscous liquid is pumped through pipes and heat exchangers into the reaction chamber. The catalyst may also be added at successive stages in the operation, or the coal may be soaked with a solution of the catalyst.

The reaction is highly sensitive to changes in temperature because of the high-molecular-weight compounds present in the coal. Great care must be taken to avoid overheating, particularly during the preheating operations; otherwise, the components of the coal that still have their original molecular structure will tend to form coke and inert products not suitable for further hydrogenation. Another difficulty lies in completing the hydrogenation reaction, for, although the coal is finely ground, the particles are solid, and contact with hydrogen is possible, therefore, only on the surface. After partial hydrogenation and reduction of oxygen compounds in the coal have occurred, the particles, aided by the action of the heavy oil, swell and partly dissolve, resulting in an almost completely liquid mass. The oil also serves to maintain the temperature uniform throughout the reaction chamber. The primary hydrogenation products are heavy, high-boiling oils, which crack, if maintained at temperatures of 450°C. (840°F.) or above, into lighter oils, gasoline, and gas. If the time of hydrogenation is controlled, the liquefied product from the coal may be obtained as light oils, gasoline, or gas, with the heavy pasting oil recovered unchanged.

Figure 12 shows a flow sheet for the hydrogenation of coal.[1] For the case of brown or young coals or those high in lignin content, different temperature and pressure conditions are usually employed in the liquid- and the vapor-phase hydrogenation steps. For example, for the liquid-phase operation, hydrogen pressures up to 700 atmos. may be employed,

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[1] LOWRY, "Chemistry of Coal Utilization," Vol. II, p. 1754, John Wiley & Sons, Inc., New York, 1945.

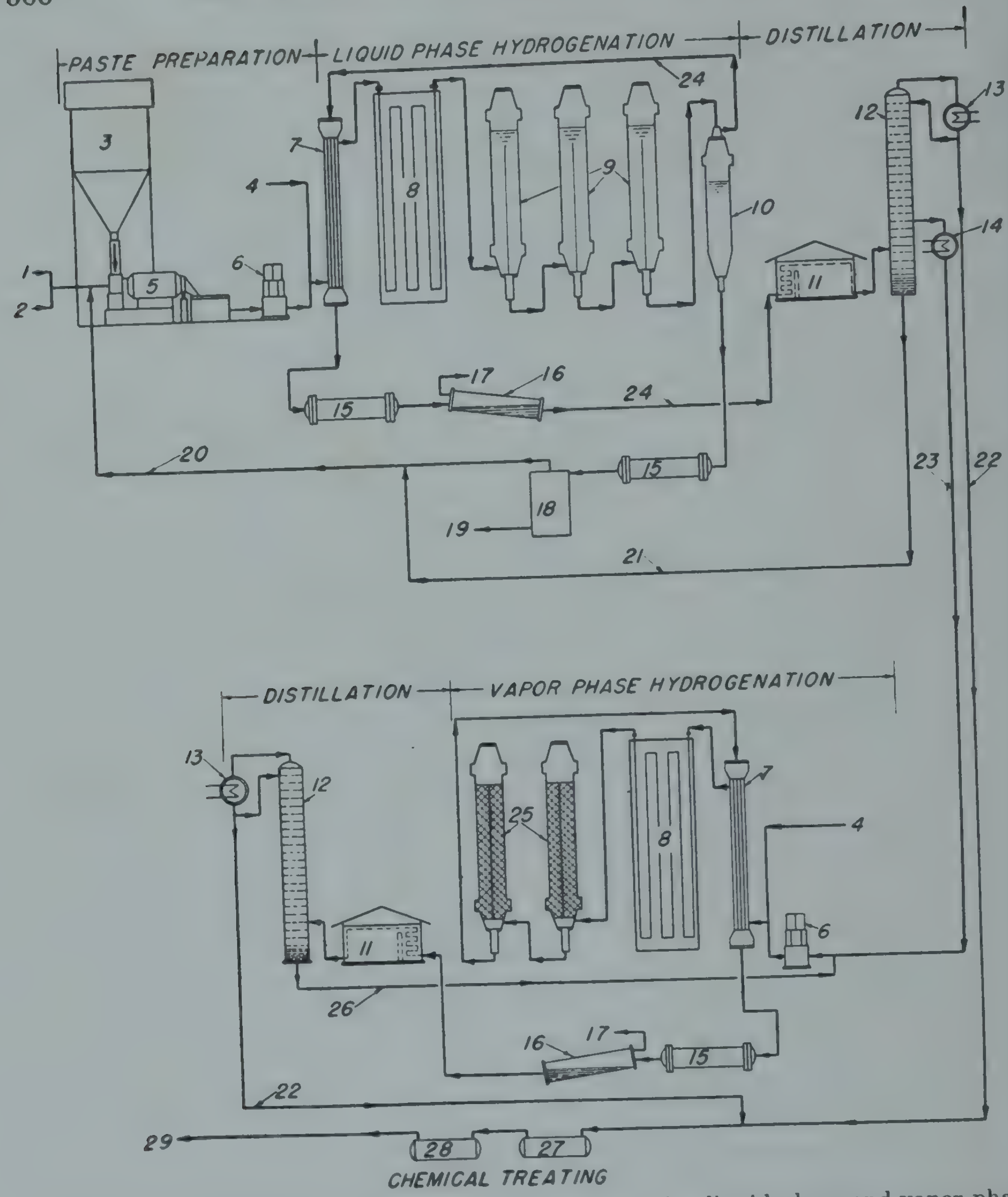

PASTE PREPARATION
LIQUID PHASE HYDROGENATION
DISTILLATION
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
DISTILLATION
VAPOR PHASE HYDROGENATION
25
26
27
28
29
CHEMICAL TREATING

FIG. 12.—Flow sheet for the hydrogenation of coal showing liquid-phase and vapor-phase steps.

1. Oil inlet.
2. Catalyst inlet.
3. Storage for clean and dry coal.
4. Hydrogen inlet.
5. Grinding mill and paste preparation.
6. High-pressure injectors.
7. Heat exchanger.
8. Gas-fired preheater.
9. Liquid-phase reaction chambers.
10. Hot catchpot or separator.
11. Furnace.
12. Distillation tower.
13. Condenser.
14. Oil cooler.
15. Condenser and cooler.
16. Cold catchpot or separator.
17. Exit gas for recycling or purification.
18. Sludge recovery.
19. Outlet for coke, ash, and catalyst.
20. Recovered or recycled heavy oil for re-hydrogenation.
21. Recycled heavy oil for pasting.
22. Gasoline or other volatile products flowing to chemical treating unit.
23. Middle oil for vapor-phase hydrogenation.
24. Crude liquid product.
25. Vapor-phase reaction chambers.
26. Recycle middle oil.
27. Acid treater.
28. Caustic treater.
29. Finished gasoline or other volatile products.

whereas in the vapor-phase step, the pressures may be confined to around 300 atmos. Referring to Figure 12, the coal is first dried, then crushed, ground, and screened so that the bulk of the coal particles are below 0.1 mm. in size. It is then mixed with catalyst and a nonvolatile oil (one boiling above about 350°C., atmospheric pressure) and made into a paste in the paste mill. High-pressure reciprocating pumps or injectors force this paste, which may contain about 35 to 50 per cent coal, into the liquid-phase hydrogenation unit. The latter consists of a heat exchanger, a gas-fired furnace, and reaction chambers or converters where sufficient time and temperature are provided for the interaction between the coal and the hydrogen. In the converters, the bulk of the coal is changed into liquid and gaseous products. The solids consisting of ash, coke, catalyst, and any other nonconvertible materials are separated from the bulk of the other products in the catchpot. A final separation of the solids from the liquid is usually made by centrifuges in the sludge-recovery unit. The chemical composition of the ash is important, for it affects the formation of deposits in the converters and the ease with which the solids can be cleanly separated from the liquid products.

In the liquid-phase hydrogenation, the catalyst may comprise about 5 weight per cent of the dry coal, and it is commonly composed of sulfur-resistant and promoted iron- and iron oxide-containing catalysts on special clays. The residue or nonliquefiable portions may be 10 to 15 per cent of the coal. This liquid-phase hydrogenation commonly occurs at around 450 to 475°C., and, as indicated, the hydrogen pressures range from about 300 to 700 atmos. From about one-third to one-half of the coal may be converted in this step to hydrocarbons boiling below approximately 400°C. A portion of this product boiling in the range of about 200 to 400°C. is commonly termed *middle oil*, and it may contain 10 to 20 per cent of phenols. Products boiling above the middle oil are recycled to the liquid-phase hydrogenation step.

The middle oil is further hydrogenated in a second, or vapor-phase, hydrogenation to convert it into hydrocarbons in the gasoline boiling range, *i.e.*, those which boil to about 200°C. at atmospheric pressure. This vapor-phase step is similar in certain respects to the liquid-phase operation except that a fixed-bed type of catalyst is used; the temperatures are usually in the range of 350 to 400°C.; and the hydrogen pressures are commonly between 200 and 300 atmos. Since all the material used in this vapor-phase operation has been distilled, there is no problem with respect to solid handling and disposal. The distillation tower removes the hydrocarbons in the gasoline or Diesel fuel range, and the higher boiling portions can be recirculated through the vapor-phase converter to be changed ultimately into lower boiling fuels. Any basic or nitrogen-containing compounds are removed by acid washing. Similarly, any remaining phenolic constituents are eliminated from the fuel by a caustic soda wash.

In hydrogenations of this type, from five to ten times as much hydrogen may be circulated as consumed. For processing young or brown coals, this consumption may be 10 to 15 cu. ft. of hydrogen per pound of coal.

All types of lignite and most bituminous coals, except those which have progressed too far in the coalification process, such as anthracite, are suitable raw materials for liquefaction. Young coals, which at present have the least value, are most suitable for high-pressure hydrogenation.

CHAPTER IX

ALKYLATION

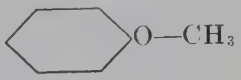
By R. Norris Shreve

I. INTRODUCTION

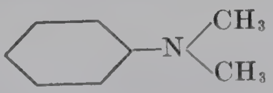
Types of Alkylated Compounds.—Alkylation may be defined as the introduction of an alkyl radical by substitution or addition into an organic compound. We also include under this procedure the introduction of an aralkyl radical, such as benzyl. Alkylation is of five general types, depending on the linkage effected:

1. Substitution for hydrogen in the hydroxyl group of an alcohol or a phenol. Here the alkyl is bound to oxygen.

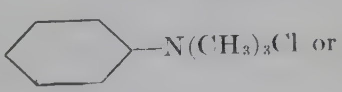
$C_2H_5O—C_2H_5$



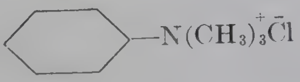
2. Substitution for hydrogen attached to nitrogen. Here the alkyl is bound to trivalent nitrogen.



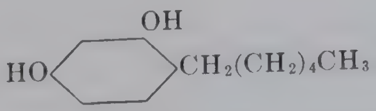
3. Addition of an alkyl halide or an alkyl ester to a tertiary nitrogen compound. Here the binding of the alkyl is to the nitrogen, and the trivalent nitrogen is often assumed to be converted to a pentavalent linkage. In reality, the nitrogen possesses four ordinary covalencies and one electrostatic bond.



or



4. Substitution for hydrogen in carbon compounds. This is nuclear alkylation when an aromatic hydrogen is substituted. The carbon of the alkyl is bound to carbon of either aliphatic or aromatic compounds. This is carbon-to-carbon alkylation.



5. Alkyl-metallic compounds. Here the alkyl is bound to the metal.

$$Pb(C_2H_5)_4$$

While the number of possible different alkyl radicals is very large, the following are the principal ones of technical importance: methyl, ethyl, propyl, butyl, amyl, and hexyl. The introduction of the aralkyl or benzyl radical, as well as the unsaturated allyl group, may also be included here, for they are technically important.

Products Derived by Alkylation.—An examination of the products obtained as a result of alkylation shows that this *unit process* is used in the making of anesthetics, antipyretics, alkaloids, antiseptics, dyes, explosives, flavors, hypnotics, intermediates, perfumes, photographic chemicals, plastics, synthetic rubber, rubber accelerators, solvents, soporifics, synthetic gasoline, etc.

Among our anesthetics, mention need be made only of ether and procaine; and, among antipyretics, acetophenetidine, antipyrine, and pyramidone. In the field of alkaloids, opium contains some codeine, but, to augment this supply, the phenolic hydroxyl of morphine is methylated. The caffeine market is partly supplied by methylation of theobromine. Anitseptics include many alkylated products that exemplify several different types of alkyl linkage, hexylresorcinol and thymol being examples of nuclear alkylation, whereas in guaiacol we find oxygen alkylation.

The alkylation process enters into dye manufacture in two ways, because dyes may be formed from alkylated intermediates, or, in a lesser number of instances, an intermediate may be subjected to alkylation as a final step. For instance, dimethylaniline is condensed with phosgene to give tetramethyldiaminobenzophenone (Michler's ketone). From this ketone are formed many dyes, such as Crystal Violet and Victoria Blue. On the other hand, the alkylation process may be almost the last step in the manfacture of a dye, for example, when the disazostilbene dye Paper Yellow 3G is ethylated to give Chrysophenine G.

Among the booster explosives, we find trinitrophenylmethylnitramine commonly called tetryl or tetralite. An outstanding example of an alkylated compound in the field of flavors is vanillin. Alkylation plays a striking part in the preparation of hypnotics, *e.g.* barbital (veronal), phenobarbital (luminal), and amytal, rendering them lipoid soluble.

Alkylation is of paramount importance in the preparation of intermediates, for the manufacture of dyes, perfumes, flavors, rubber accelerators, medicinals, and the like. Among alkylated intermediates, dimethylaniline has probably the most extensive and varied application. Other important members of this class are benzylethylaniline, benzylmethylaniline, diethylaniline, dianisidine, *m*-diethylaminophenol, and trimethylphenylammonium chloride. Perfumes include numerous instances of alkylated compounds, such as nerolin (β-naphthyl methyl ether) and artificial musk. As a photographic developer, metol (N-methyl-*p*-aminophenol sulfate) has long held an important place. Rubber accelerators include such compounds as thionex (tetramethyl thiuram sulfide).

In the field of solvents, many new alkylated compounds have been synthesized, these being principally complex ethers of ethylene glycol, *e.g.*, ethylene glycol ethyl ether and diethylene dioxide, or *p*-dioxane.

Alkylation plays an important role in the production of synthetic rubber of the GR-s type, this unit process being employed for the preparation of ethylbenzene from which styrene is derived.

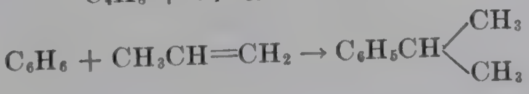
The petroleum industry first obtained gasoline by straight-run distillation. Next the longer molecules were cracked. Now gasoline is being synthesized on a large scale. For this purpose, the most important reaction in all probability is an alkylation wherein olefins, by the aid of catalysts, are made to combine with other molecules such as isoparaffins and aromatics. Such syntheses are discussed in several chapters of this volume and are given consideration here particularly to exemplify reactions involving alkyl bound to carbon.

These and other reactions such as for synthetic rubber, methanol, ethanol, acetone, and solvents have brought on the synthetic period of the petroleum industry.

II. ALKYLATING AGENTS

Olefins.—In the presence of a metal halide, hydrogen fluoride, or sulfuric or phosphoric acid the olefins are able to enter into syntheses involving alkylation. During the course of the reaction, there is a transfer of hydrogen from the carbon of an aliphatic, aromatic, or hydroaromatic compound to the carbon of the olefin, thereby forming an alkyl radical. These reactions may be represented thus:

$$C_4H_8 + C_4H_{10} \rightarrow C_4H_9{\cdot}C_4H_9$$



$$C_6H_6 + CH_3CH{=}CH_2 \rightarrow C_6H_5CH\begin{matrix}CH_3\\CH_3\end{matrix}$$

$$C_6H_6 + CH_2{=}CH_2 \rightarrow C_6H_5C_2H_5$$

Ipatieff employed ethylene, propylene, and the higher olefins in similar reactions and obtained mono- and polyalkylated derivatives. In general, the olefins of higher molecular weight, *e.g.*, amylene, and most branched chains, *e.g.*, *tert*-butyl chloride, react more readily than do propylene and ethylene.

Alcohols.—Methanol and ethanol are among the oldest and most widely employed reagents for technical alkylation. This is largely a result of their availability, relatively low cost, and the excellent yields that frequently result from their use. In practically every case, a catalyst is necessary to cause the alkylation to proceed smoothly, and, in many instances, this is a mineral acid. Alcohols are used in the manufacture of ethers, such as ordinary ethyl ether, isopropyl ether, Carbitol, Cellosolve and naphthyl methyl ether. It should be noted that although naphthols react on alcohol in the presence of a mineral acid, the aryl alkyl ethers cannot be formed by this reaction in the case of phenols.

Dimethylaniline is made from aniline and methanol in the presence of a small amount of sulfuric acid, whereas diethylaniline is prepared from aniline and ethyl alcohol using hydrochloric acid. The ethylation does not proceed so completely as the methylation.

The alcohols are employed to effect the replacement of aromatically bound halogen atoms by heating in the presence of an alkali. In this way, *p*-nitrophenetole and *o*-nitroanisole are made by treating *p*-nitrochlorobenzene with ethanol and *o*-nitrochlorobenzene with methanol.

The lower alcohols have also been employed extensively for the catalytic vapor-phase synthesis of alkylamines and for the alkylation of phenols.

The preceding describes the use of alcohols as alkylating agents involving oxygen and nitrogen linkages. They also serve for carbon-to-carbon alkylations,[1] wherein the alcohol is first esterified with sulfuric acid and this ester reacted with an aromatic compound. An example of such an alkylation is the preparation of cumene from isopropyl alcohol, sulfuric acid, and benzene. The reaction is quite similar to alkylation with olefins, using sulfuric acid or phosphoric acid as the catalyst.

Alkyl Halides.—The alkyl halides are probably the most commonly used laboratory alkylating agents and are also employed for certain manufacturing processes, as in making lead tetraethyl. Most of the lower alkyl halides are now abundant and cheap because of recent developments relating to (1) addition of HCl to olefins and (2) chlorination of paraffins. These reactions, which are discussed at length under Halogenation, may be represented as follows:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$$
$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$

The tertiary alkyl halides react vigorously and, in the case of *tert*-amyl chloride, can alkylate phenols without the intervention of a catalyst. Methyl iodide is used in the preparation of such methylated products as Pinaverdol and other sensitizing dyes, which possess a pentavalent nitrogen.

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[1] Günther, U. S. 1,670,505 (1928); Verley, U. S. 1,756,575 (1930).

Phenols, such as *o*-nitrophenol (*cf.* Acetophenetidine), are alkylated by heating with alkyl chlorides in the presence of aqueous alkali. Ethyl chloride serves as the alkylating agent in making diethylamine (*q.v.*) by heating with ammonia in an absolute alcohol medium in an autoclave. It is also employed for the carbon alkylation leading to barbital and for the alkylated metals, *e.g.*, lead tetraethyl (*q.v.*). Methyl and ethyl bromides or iodides react very smoothly and, in spite of their cost, find application in the field of dyes and medicinal products, *e.g.*, pyramidone and antipyrine, for the preparation of simple and mixed ethers and for the alkylation of phenols and amines. Low-cost methyl chloride is also used. Allyl bromide is employed for making diallylbarbituric acid (dial).

Alkyl Sulfates.—In recent years, the alkyl sulfates have been growing in technical importance. Dimethyl sulfate has long been available at reasonable cost, and diethyl sulfate is now similarly obtainable. The dialkyl sulfates are usually caused to react in the presence of an alkali, thus producing the alkali alkyl sulfate.

In certain cases such as are detailed under Anisole (*q.v.*), the second methyl of the dimethyl sulfate enters into reaction. Dimethyl sulfate is employed in the methylation leading to alkyl oxygen compounds, *e.g.*, β-naphthyl methyl ether, etc.; to alkyl nitrogen compounds *e.g.*, caffeine and acriflavine; and to many others.

Diethyl sulfate, although reacting not quite so smoothly as dimethyl sulfate, is highly recommended[1] for various ethylations, *e.g.*, those yielding β-naphthyl ethyl ether, phenetole, diethylaniline, and Cellosolve (*q.v.*). Both ethyl groups of diethyl sulfate can be made to react when the reaction system is practically anhydrous. Only one ethyl group reacts, however, in the presence of substantial amounts of water. In alkylations with dimethyl sulfate or diethyl sulfate, the use of autoclaves can generally be avoided.

In certain instances, monoalkyl acid sulfate may be regarded as the active alkylating reagent, as, for example, in the formation of ether from ethyl alcohol and sulfuric acid.

Aralkyl Halides.—Benzyl chloride is almost universally used for the introduction of the benzyl group, for instance, in the preparation of benzylethylaniline from ethylaniline. In actual practice, the benzylethylaniline is usually obtained by treating a mixture of ethylaniline and diethylaniline and fractionating. Benzyl chloride is also used in the preparation of benzyl cellulose.

Arylsulfonic Alkyl Esters.—Among the arylsulfonic alkyl esters, we find of importance the methyl or ethyl ester of *p*-toluenesulfonic acid and also the higher alkyl esters. These compounds are found suitable for the alkylation of certain amines for which the alcohols are not satisfactory. Under Codeine (*q.v.*) is described the use of methyl benzenesulfonate and of methyl toluenesulfonate in the preparation of tetraalkylammonium compounds. Sekera and Marvel report favorably on the preparation and use of the higher alkyl (C_{10} and above) esters of *p*-toluenesulfonic acid and *p*-bromobenzenesulfonic acid as alkylating agents for making alkylamines, such as N-butyllaurylamine, N-butylcetylamine, and N-butyldicetylamine.[1] These higher alkyl esters of *p*-toluenesulfonic acid are more satisfactory than the sluggish higher alkyl halides and are more easily obtained than the higher alkyl sulfates.

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[1] Cade, *Chem. Met. Eng.*, **29**, 319–323 (1923).

Alkyl Quaternary Ammonium Compounds.—These have long been applied in certain special fields, and their further use may well be warranted in many instances. A detailed specific example of this application is given under Codeine, where the preparation and use of phenyltrimethylammonium chloride ($C_6H_5N(CH_3)_3Cl$) is described. These quaternary alkyl substances have also been recommended for alkylations leading to phenetole, antipyrine, pyramidone, acriflavine, and caffeine.

Reductive Alkylation[2] with Aldehydes or Ketones and Hydrogen.—This procedure is particularly applicable to nitrogen alkylation, wherein primary or secondary aromatic or aliphatic amines or aromatic nitro compounds react with hydrogen and a carbonyl compound (aldehyde or ketone) in the presence of a hydrogenation catalyst (Raney nickel or platinum black) and a condensing agent (alkali-metal salt of weak organic acid as sodium acetate) to give good yields of the nitrogen alkyl derivatives. The reductive alkylation is frequently carried out in an alcoholic solution from 10 to 40°C. and under a hydrogen pressure of 2 to 4 atmos. In large batches, cooling may be helpful to control the reaction. Examples of products made in this manner are (1) N-ethylaniline from either acetaldehyde and aniline or nitrobenzene and (2) N-benzyl-alpha-naphthylamine from benzaldehyde and alpha-naphthylamine. One of the advantages of this method is the suppression of the formation of tertiary amines when reacting on a primary amine.

Miscellaneous Alkylating Agents.—Noller and Dutton have recommended the trialkyl phosphates for alkylation and have discussed their preparation.[3] Ethers are formed by using one equivalent of the trialkyl phosphate per mole of phenol. The yields of ether in the accompanying table are based on the amount of the alkyl radical available and hence are a measure of the relative alkylating ability of the various esters.

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[1] SEKERA and MARVEL, *J. Am. Chem. Soc.*, **55,** 345 (1933); *cf.* SLOTTA and FRANKE, *Ber.*, **63B,** 678–691 (1930).

[2] Emerson, U. S. 2,298,284 (1942); many literature references; *J. Am. Chem. Soc.*, **60,** 2023–5 (1938); **61,** 3145 (1939); **62,** 69–70 (1940); **63,** 972–4 (1941).

[3] NOLLER and DUTTON, *J. Am. Chem. Soc.*, **55,** 424 (1933); *cf.* Consortium für Electrochem. Ind., Brit. 433,927 (1935).

TABLE I.—YIELDS OF PHOSPHATES AND PHENOL ETHERS

Ester	Phosphates		Phenol ethers	
	Yield, %	B.p., °C.	Yield, %	B.p., °C.
Ethyl sulfate	....	....	73.0	168–170
Ethyl phosphate	51.7	104–107 (16 mm.)	21.6	167–170
n-Propyl phosphate	63.5	128–134 (15 mm.)	Not run	
n-Butyl phosphate	74.0	160–162 (15 mm.)	39.0	204–211
sec-Butyl phosphate	44.0	119–129 (8–12 mm.)	18.7	188–198
n-Amyl phosphate	63.7	158–163 (6 mm.)	15.0	125–128 (25 mm.)

Riedel describes the methylation of *p*-aminophenol to metol, using formaldehyde followed by reduction with activated aluminum.[1]

Carbon-bound alkyl groups are frequently introduced by special procedures such as in the preparation of hexylresorcinol (*q.v.*) by reduction of a ketone derivative and in the making of thymol[2] by the rearrangement of isopropyl *m*-tolyl ether.

III. TYPES OF ALKYLATION

The five different types of alkylation treated in this chapter are sharply defined from a structural viewpoint. However, the linkage of alkyl to oxygen, nitrogen, carbon, or a metal can, in many instances, be effected by the same alkylating agent, *e.g.*, ethyl chloride. Naturally, there is some variation in the conditions under which such a reagent is employed to produce these various compounds.

Alkyl Bound to Oxygen.—The compounds of this class are generally prepared by substituting an alkyl group for a hydrogen in the hydroxyl group of an alcohol or a phenol. Typical compounds containing this alkylation linkage are the following:

Aliphatic Ethers:
- Cellulose ethers
- Ethylene glycol ethers:
  - Carbitol
  - Cellosolve
- Ethyl ether
- Isopropyl ether

Phenol Ethers and Derivatives:
- Acetophenetidine
- *o*-Anisidine
- Anisole
- Chrysophenine G
- Codeine (methyl ether of morphine)
- *o*-Dianisidine
- Ethylmorphine
- Guaiacol
- β-Naphthyl methyl ether
- *o*-Nitroanisole
- Phenetole
- Vanillin

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[1] Riedel, Ger. 406,533 (1922).

[2] NIEDERL and NATELSON, *J. Am. Chem. Soc.*, **54**, 1063–1070 (1932); SOWA, HINTON, and NIEUWLAND, *ibid.*, 2019; NIEDERL and STORCH, *ibid.*, **55**, 284–294 (1933).

Aliphatic Ethers.—The aliphatic ethers used in industry are made usually by the action of sulfuric acid upon an alcohol. Here the active alkylating agent is the monoalkyl sulfate produced by the dehydrating[1] action of the sulfuric acid. Ethyl ether and isopropyl ether[2] are thus prepared. Wuyts and Lacourt, studying the action of sulfuric acid upon propyl alcohol, assert that ethylenic compounds are intermediate products in this method of ether formation.[3]

For mixed ethers, the Williamson synthesis is particularly applicable:

$$C_2H_5ONa + CH_3I \rightarrow C_2H_5OCH_3 + NaI$$

Often, a cheaper and sufficiently satisfactory procedure is to react an alcohol and an alkyl halide in the presence of alkali. Mixed ethers can also be made by certain aspects of the Grignard synthesis, as, for example,

$$C_2H_5MgBr + BrCH_2OCH_3 \rightarrow C_2H_5CH_2OCH_3 + MgBr_2$$

The cellulose ethers are generally made by the action of alkyl or aralkyl halides on alkali cellulose. The reactions are carried out under pressure at about 100°C. In connection with ethers, reference should be made to the examples in this chapter describing the preparation of Carbitol (diethylene glycol ethyl ether), Cellosolve (ethylene glycol ethyl ether), and ethylcellulose.

Phenol Ethers.—The phenol ethers are manufactured frequently by the reaction of the sodium phenoxide with an alkyl halide, alkyl sodium sulfate, or dialkyl sulfate or the alkyl ester of toluenesulfonic acid (*cf.* Anisole and Vanillin). Under Acetophenetidine is detailed a method whereby good yields are obtained by ethylating *p*-nitrochlorobenzene with alcohol potash in the presence of potassium sulfite. The naphthol ethers[4] are a little easier to form and result, for example, by heating together naphthol, methanol, and sulfuric acid.

Alkaloids.—Some of the most difficult oxygen alkylations are those involving the alkaloids, where the alkylation is often carried out to replace the hydrogen of the hydroxyl group in the presence of the tertiary nitrogen of the alkaloid. The best commercial example of the work that has been done with this particular group of compounds is the formation of codeine by the alkylation of the phenolic hydroxyl in morphine. Details of this alkylation with quaternary ammonium compounds are given under Codeine. Such procedure is also used for theobromine, antipyrine, etc.

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[1] SENDERENS, *Compt. rend.*, **176,** 813–816 (1923); **179,** 1015–1019 (1924); **181,** 698–700 (1925).

[2] Mann, U. S. 1,482,804 (1924).

[3] WUYTS and LACOURT, *Bull. soc. chim. Belg.*, **39,** 157–173 (1930).

[4] GATTERMANN, *Ann.*, **244,** 73 (1882); WITT and SCHNEIDER, *Ber.*, **34,** 3173 (1901)

Alkyl Bound to Trivalent Nitrogen.—In this division, the compounds may be considered as being derived by the substitution of an alkyl group for a hydrogen attached to a trivalent nitrogen. Examples of such substitutions are as follows:

- Aliphatic Alkylamines:
  - Diethylamine
  - Dimethylamine
  - Adrenaline (side chain)
  - Methylamine
  - Procaine (side chain)
  - Tetramethyl thiuram sulfide
  - Trimethylamine
- Heterocyclic alkylamines:
  - Pyramidone
  - Antipyrine
- Aromatic Alkylamines:
  - Benzylethylaniline
  - *m*-Diethylaminophenol
  - Diethylaniline
  - *m*-Dimethylaminophenol
  - Dimethylaniline
  - Metol
  - Tetryl
- Alkaloids:
  - Caffeine
  - Codeine
  - Ethylmorphine

Aliphatic Alkylamines.—In the aliphatic series, dimethyl sulfate is a particularly valuable alkylating agent, which reacts easily with amines in nitrobenzene, alcohol, chloroform, or other solutions—often without any external heating. Methyl iodide also reacts readily, but the methyl bromide requires some heating. In this series, the tendency commercially is to alkylate with the alcohol, often employing special procedures such as are exemplified by the making of methylamines from ammonia and excess methanol in the vapor phase and in contact with alumina at 400°C. Reference should be made to the discussion of diethylamine for details of the alkylation, where ammonia is heated with ethyl chloride in presence of absolute ethyl alcohol.

In a number of substances, such as adrenaline and procaine, where alkyl groups occur in a side chain, the actual alkylation is usually effected in simpler compounds such as methylamine and diethylamine, which are then condensed onto the main product. Similarly, the alkyl groups of tetramethyl thiuram sulfide, $(CH_3)_2N(S)CSC(S)N(CH_3)_2$, are introduced by dimethylamine.

Aromatic Alkylamines.—In the aromatic series, the use of methanol and sulfuric acid is exemplified in the commercial process for making dimethylaniline. (*cf.* Dimethylaniline). The sulfuric acid forms methyl sulfate, and this is to be compared with the alkylation procedure resulting in the formation of ethyl ether from alcohol and sulfuric acid Diethylaniline is also made similarly, employing ethyl alcohol, but here sulfuric acid cannot be used because ethyl ether would be formed; consequently, hydrochloric acid is the catalyst chosen.

Carleton and Woodward claim an improvement in making ethyl- and diethylaniline from aniline and ethyl alcohol, by using with the alcohol less than a molecular equivalent (per mole of amine) of either ethyl chloride or hydrogen chloride.[1] In both cases, the reactants are heated under pressure and at a temperature of 180 to 185°C.[2]

Benzylethylaniline is an important dye intermediate which is made by the action of benzyl chloride on ethylaniline. Martin and McQueen find that the addition of benzyl chloride at about the rate that it is used up in the reaction is advantageous.[3] Livingston carries on the benzylation in toluene or other hydrocarbon solvent and in the presence of an acid binding agent (Na_2CO_3).[4]

To avoid some of the ordinary by-products arising when dimethylaniline is made from methanol with sulfuric acid as a catalyst, Britton and Williams use from 1 to 2 per cent of methyl bromide by weight and 3 to 4 moles of methanol per mole of aniline.[5] The reactants are heated in a stirred iron autoclave for approximately 16 hr. at from 230 to 240°C. and under a corresponding pressure of about 700 lb. Most of the methyl bromide can be recovered as the quaternary compound phenyltrimethylammonium bromide. Indeed, this quaternary compound can be introduced as the catalyst, as it decomposes under the conditions of the alkylation. The reaction may be formulated:

$$C_6H_5NH_2 + 2CH_3OH + CH_3Br \rightarrow C_6H_5N(CH_3)_3Br + 2H_2O$$
$$C_6H_5N(CH_3)_3Br \rightarrow C_6H_5N(CH_3)_2 + CH_3Br$$

The use of aromatic sulfonic acids[6] as catalysts in the methylation of primary aromatic amines by aliphatic alcohols has been reported.

When alkylating primary, secondary, or tertiary aromatic alkylamines much heat usually is evolved; this can be controlled by initial cooling or dilution. Such heat development is more pronounced when using dimethyl sulfate and alkyl toluenesulfonic esters than with alkyl halides, but even the latter must be handled carefully. To secure the best yields, no water must be present; if water is present, it will react with the dimethyl sulfate, yielding methyl sulfate, which will, in turn, form a salt with the amine and withdraw it from alkylation.

Dimethyl sulfate has been employed successfully in the methylation of *p*-aminophenol to metol, but special precautions must be taken to secure good yields.[7] The almost quantitative monalkylation of *p*-aminophenol is claimed by Zimmerli by first forming an aldehyde amine before treating with the methylating agent.[1] With the use of furfural and dimethyl sulfate, the reaction in dry chlorobenzene as a solvent can be represented by the following equations:

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[1] Carleton and Woodward, U. S. 1,994,851; 1,994,852 (1935).

[2] This use of hydrochloric acid as a catalyst in the making of ethyl- and diethylaniline has been known for some time.

[3] Martin and McQueen, U. S. 1,887,772 (1932).

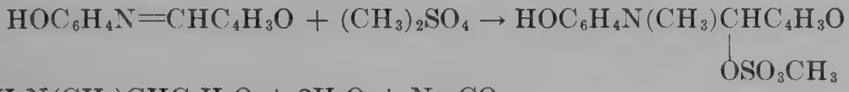
[4] Livingston, U. S. 1,854,553 (1932).

[5] Britton and Williams, U. S. 1,794,092 (1931).

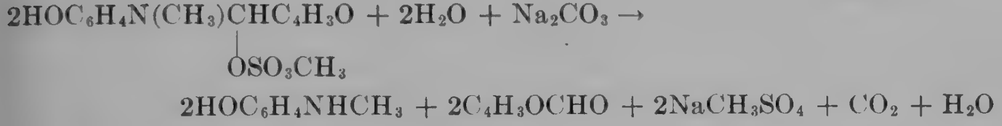
[6] Laptev and Khaikin, Russ. 42,553; *C. A.* **31,** 7067 (1937).

[7] SCHWYZER, "Die Fabrikation pharmazeutischer und chemischtechnischer Produkte," pp. 223–226, Verlag Julius Springer, Berlin, 1931.

$$HOC_6H_4NH_2 + C_4H_3OCHO \rightarrow HOC_6H_4N{=}CHC_4H_3O + H_2O \qquad (1)$$



$$HOC_6H_4N{=}CHC_4H_3O + (CH_3)_2SO_4 \rightarrow HOC_6H_4N(CH_3)\underset{\substack{|\\ OSO_3CH_3}}{C}HC_4H_3O \qquad (2)$$



$$2HOC_6H_4N(CH_3)\underset{\substack{|\\ OSO_3CH_3}}{C}HC_4H_3O + 2H_2O + Na_2CO_3 \rightarrow$$
$$2HOC_6H_4NHCH_3 + 2C_4H_3OCHO + 2NaCH_3SO_4 + CO_2 + H_2O \qquad (3)$$

Compounds containing alkyl attached to trivalent nitrogen are unusually important in the dye field. Almost invariably, the presence of this alkyl group attached to nitrogen is dependent upon the use of alkylated aromatic amines, such as dimethylaniline, as intermediates. Among the dyes so formed are Auramine, Malachite Green, Methyl Violet, Crystal Violet, and Methylene Blue.[2] In the early stages of the development of the dye industry, some nitrogen alkylation was practiced, wherein, after the formation of the central dye-ring, alkylation was effected by the use of the alkyl halide in the presence of caustic soda (*cf.* Hoffman's Violet, No. 679, and related dyes in Colour Index; Society of Dyers and Colourists, Bradford, England).

Alkaloidal Amines.—The presence of a methylated tertiary nitrogen is fairly common among alkaloids, such as morphine, codeine, caffeine, and theobromine. As caffeine differs from theobromine by having one more nitrogen methylated, it is made by treating theobromine with dimethyl sulfate in the presence of sodium ethylate or by boiling in an alkaline alcoholic solution with methyl *p*-toluenesulfonate.

Heterocyclic Amines.—The pyrazolones—pyramidone[3] and antipyrine—are prepared by using methyl bromide in an acid medium as the alkylating agent whereby the formation of by-products is lessened. Adkins and Cramer effect the N-alkylation of heterocyclic amines, such as piperidine, by alcohols, *e.g.*, 1-butanol in the presence of a nickel catalyst and hydrogen or nitrogen under high pressure.[4]

Alkyl Bound to Pentavalent Nitrogen.[5]—In this division, alkylation is effected by addition, the trivalent nitrogen becoming pentavalent. There are not included here those tertiary alkyl compounds wherein the nitrogen becomes pentavalent by simple salt formation.

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[1] Zimmerli, U. S. 1,987,317 (1935).

[2] *Cf.* Shreve, "Dyes Classified by Intermediates," Reinhold Publishing Corporation, 1922, for further details.

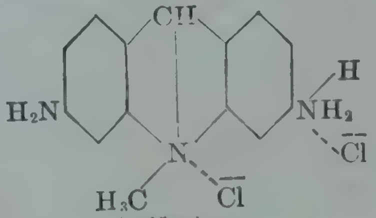
[3] Schwyzer, *op. cit.*, pp. 164–172.

[4] Adkins and Cramer, U. S. 2,058,547 (1936).

[5] See p. 563.

The preparation of this type of compound is relatively simple, in that an alkyl halide, an alkyl sulfate, or an alkyl ester is added to a tertiary amine. Details for the making of the quaternary ammonium compounds—phenyltrimethylammonium chloride and phenyltrimethylammonium tolysulfonate—are later described under Codeine. These substances are excellent methylating agents, particularly when it is desired to methylate a phenolic hydroxyl in the presence of a tertiary nitrogen.

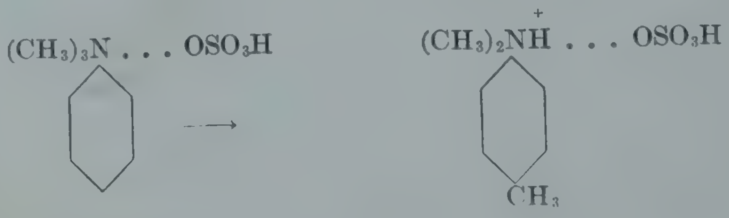
Acriflavine, a widely used medicinal dye, containing a methylated pentavalent nitrogen is prepared by methylating the tertiary ring nitrogen in diaminoacridine by either dimethyl sulfate or methyl *p*-toluenesulfonate in nitrobenzene or a benzene solution. Although generally the two amino groups have been protected by acetylation prior to the methylation of the ring nitrogen, this step is not necessary. The methylated product is converted by hydrochloric acid to the chloride monohydrochloride which is known as Acriflavine.[1]



Acriflavine

Alkyl Bound to Carbon.—These compounds may be considered as being derived by the substitution of an alkyl group for hydrogen in carbon compounds. Examples are "alkylate" for synthetic gasoline, ethylbenzene for styrene entering into the manufacture of plastics and rubber, hexylresorcinol, thymol, barbital, and other barbituric acid alkyl derivatives. This type of alkylation is frequently referred to as alkylation of hydrocarbons, and many of the instances are nuclear alkylations. In the main, the same reagents are employed as for the other classifications with much recent emphasis upon olefins particularly for alkylate for petroleum (*q.v.*)

In some instances, an alkyl bound to nitrogen or to oxygen may wander to the nucleus. For example, aniline is converted to dimethylaniline by heating to around 205° with methanol and a small amount of sulfuric acid; if the temperature is raised to around 250 to 300°, considerable nuclear alkylation takes place, the reaction probably being as follows:



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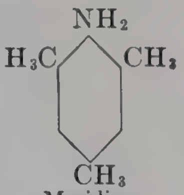
[1] SHREVE, *loc. cit.* pp. 82–83.

In the presence of excess methanol and at higher temperature (300 to 350°), mesidine as well as the mono- and dimethyl derivatives are formed.

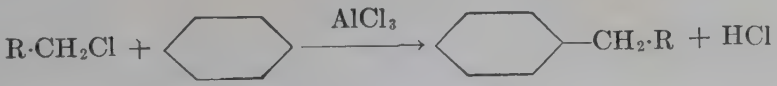


Mesidine

A similar wandering of the ethyl group in the case of diethylaniline has been studied by Johnson, Hill, and Donleavy.[1]

The nuclear alkylations that would lead to the commercially important thymol have been reported.[2] Wagner has pointed out how nuclear methylations can be carried out by the aid of formaldehyde followed by reduction and has studied the intermediate products formed.[3] This procedure leads to N-methylation of alkylanilines if the initial condensation products are promptly reduced, whereas the alkyl-*p*-toluidines (nuclear alkylation) are obtained in every case where the intermediate bases were allowed to precipitate and then separated and reduced.

Alkylation logically overlaps with other reactions. Thus, the condensation of alkyl or aralkyl halides according to the Friedel-Crafts synthesis is a form of nuclear alkylation for the preparation of aromatic compounds.



To avoid duplication, such alkylations are discussed under the Friedel-Crafts reaction when a metal halide is used as the condensing agent. When, however, the alkylations are catalyzed by other agents, *e.g.*, mineral acids, they are discussed here. Similarly, carbon linkage alkylation includes the Wurtz reaction for the preparation of aliphatic compounds.

$$CH_3Br + 2Na + BrC_2H_5 \rightarrow CH_3{\cdot}C_2H_5 + 2NaBr$$

Alkylations with Olefins.[4]—Reactions involving olefins may be represented as follows:

$$R'H + RCH{=}CHR \rightarrow RR'CHCH_2R$$

where R is either a hydrogen atom or a monovalent radical, *e.g.*, methyl or ethyl. Such reactions are presented under olefins, (page 565) and under alkylate for the petroleum industry, (page 599). Alkylation of RH with olefins frequently involves addition of R at one of the doubly bound carbon atoms and hydrogen at the other although sometimes the alkyl wanders. In such alkylations, the olefins can be made to attach to a considerable variety of other compounds, thus forming (1) longer chain compounds of the paraffin and isoparaffin series; (2) mono- or polyalkylated aromatics; or (3) mono- or polyalkylated naphthenes (alicyclics).

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[1] Johnson, Hill, and Donleavy, *Ind. Eng. Chem.*, **12**, 636–642 (1920).

[2] Niederl and Storch, *J. Am. Chem. Soc.*, **55**, 284 (1933); Smith, *ibid.*, 849.

[3] Wagner, *J. Am. Chem. Soc.*, **55**, 724 (1933).

[4] Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, 1936; Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, 1937.

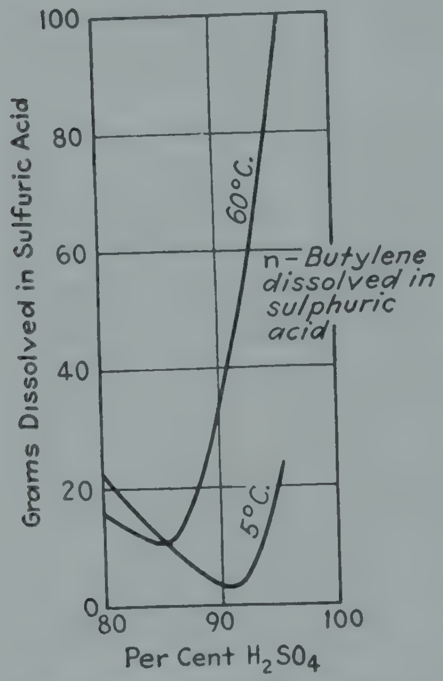
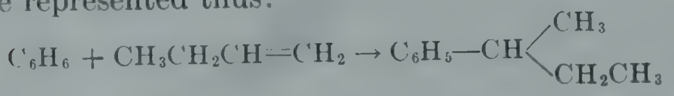


FIG. 1.—Solubility of butene-1 in sulfuric acid. (*After Ipatieff.*)

Olefin Alkylations of Benzene Catalyzed by Acids.—Benzene can be alkylated by olefins in the presence of strong sulfuric acid as shown by Ipatieff, Corson, and Pines.[1] Thus, dodecene, nonene, octene, pentene and butene (isobutylene and butylene-1), and propylene as well as ethylene have been employed for the alkylation of benzene. Ethylene needs a catalyst to give satisfactory yields of ethylbenzene. Octene also gives good yields of the mono-, di-, and trioctylbenzenes, and propylene and butylenes give high yields of alkyl derivatives. Accompanying the alkylation, some esterification occurs with the formation of the dialkyl esters of sulfuric acid, particularly with weaker sulfuric acids. In their presence, the reaction product cannot be distilled satisfactorily, since these esters decompose and form tarry products at about 120 to 130°C. However, the presence of phosphoric acid[2] causes decomposition of such esters so that the distillation can be effected without tar formation.

The nature of the alkylating action of normal butylene (butene-1) upon benzene[3] in the presence of sulfuric acid at 5 and 60°C. follows from Fig. 1, which gives the solubility data for butylene in H_2SO_4. The stronger the sulfuric acid the further the alkylation proceeds and the higher is the boiling point of the product. The primary reactions may be represented thus:



$$C_6H_6 + CH_3CH_2CH{=}CH_2 \rightarrow C_6H_5{-}CH\begin{matrix} \diagup CH_3 \\ \diagdown CH_2CH_3 \end{matrix}$$ and polyalkylated products.

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[1] IPATIEFF, CORSON, and PINES, *J. Am. Chem. Soc.*, **58**, 919 (1936); and numerous other references (see Chap. XII).

[2] Ipatieff, U. S. 2,006,695; 2,639,798 (1937).

[3] IPATIEFF, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, 1936.

The action of aluminum chloride facilitates many alkylations but is also considered in Chap. XII, The Friedel-Crafts Reaction. Paraffins, benzene,[1] toluene, and xylenes are alkylated by olefins and cyclopropane, in the presence of aluminum chloride. Usually hydrogen chloride is also needed (see alkylate for petroleum).

It cannot be overemphasized that the action of aluminum chloride is quite varied in the products that it may cause to be formed because polymerization, isomerization, dealkylation, etc., can occur concurrently. Although it is not so effective an initial alkylating agent as sulfuric acid, aluminum chloride is, however, a more effective agent to dealkylate the polyalkyl aromatics, with formation of lower alkyl aromatics.

Alkyl Bound to a Metal.—The alkyl group may be caused to unite with metals, such as lead, mercury, zinc, magnesium, and arsenic. The examples of this type of alkylation, which are later described, are lead tetraethyl and merthiolate. The intermediate in the formation of merthiolate—ethylmercuric chloride—is also being used as a fungicide. Among the lethal poison gases is ethyldichloroarsine ($C_2H_5AsCl_2$), which is prepared by the following reactions:

$$C_2H_5Cl + Na_3AsO_3 \rightarrow C_2H_5AsO_3Na_2 + NaCl \qquad (1)$$

$$C_2H_5AsO_3Na_2 + H_2SO_4 \rightarrow C_2H_5AsO_3H_2 + Na_2SO_4 \qquad (2)$$

$$C_2H_5AsO_3H_2 + SO_2 + H_2O \rightarrow C_2H_5AsO_2H_2 + H_2SO_4 \qquad (3)$$

$$C_2H_5AsO_2H_2 \rightarrow C_2H_5AsO + H_2O \qquad (4)$$

$$C_2H_5AsO + 2HCl \rightarrow C_2H_5AsCl_2 + H_2O \qquad (5)$$

IV. FACTORS CONTROLLING ALKYLATION

Concentration.—The concentration of the reagents in alkylation is often high, particularly when alcohols are the alkylating agents, as, for example, when methanol and aniline are treated under pressure in the presence of a small amount of sulfuric acid. On the other hand, it is advantageous frequently to dilute certain energetic alkylating agents in order better to control the reaction; this is done when alkylating with alkyl halides or with dialkyl sulfates. In vapor-phase alkylations, usually no diluent is needed (*cf.* Effect of Ratio of Reactants).

Temperature.—When such alkylating agents as methanol or ethyl alcohol or the alkyl halides are employed, a much higher temperature is necessary than that required with dimethyl sulfate or diethyl sulfate or even methyl *p*-toluenesulfonate. As is described later, the methylation of aniline to dimethylaniline will take place around 200°. Alkylations that are carried on in the vapor phase call for much higher temperatures —around 400°—as when phenol is methylated with methanol by passing the vapors over an alumina catalyst or when methylamines are formed by conducting methanol and ammonia in the vapor phase over an alumina catalyst. When isoparaffins are alkylated with olefins, ordinary temperature is employed with HF catalyst, but refrigeration is required with H_2SO_4 catalyst.

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[1] BERRY and REID, *J. Am. Chem. Soc.*, **49**, 3142–3149 (1927).

A number of alkylating reactions are exothermic, as for example, when aminoantipyrine is methylated with methyl bromide to give pyramidone, and here cooling is advisable in the early stages of the methylation.

Increased temperature frequently causes migration of alkyl groups to an aromatic nucleus: Dimethylaniline sulfate gives N-methyl-*p*-toluidine in this manner.

Pressure.—In numerous instances, pressure is necessary to keep reactions in the liquid phase. In making petroleum alkylate by the thermal procedure, in the N-methylation of aniline by methanol giving dimethylaniline, and in some of the C—C alkylations leading to alkylated aromatics, pressure is needed to maintain the liquid state at the temperature required.

Solvents.—Alcohols, paraffins, chloroform, benzene, or nitrobenzene are used as solvents in alkylating procedures. As a rule, though not invariably, they should be anhydrous. The use of a solvent is for two purposes, not only to lessen the vigor of some reactions but also to cause products or by-products to crystallize out. For instance, when dimethyl sulfate is employed for certain alkylations, it is dissolved in benzene and added to an alcoholic solution of the sodium phenoxide derivative to be alkylated. In the presence of these solvents, sodium methyl sulfate is very little soluble and is precipitated out. This procedure tends to give good yields. Similar conditions are applied to other alkylating agents.

Alkylations in Liquid or Vapor Phase.—Although most alkylations are carried on in the liquid phase, some of the newer procedures are conducted in the vapor phase, as are described under Catalysis.

Catalysis.—In alkylation, catalysis[1] becomes more and more important each year as further research brings an increasing number of catalysts into use. In reviewing this subject, Ipatieff makes the following classification:

1. We may view the catalyst as a reaction multiplier. Here the catalyst actually enters into the reaction, forming an unstable intermediate compound with the reacting substance. As the intermediate compound decomposes in the course of the reaction, the catalyst is continually regenerated.

2. Many catalysts act in an unknown manner. Here, the formation of the intermediate compound is doubtful, and the chemical mechanism

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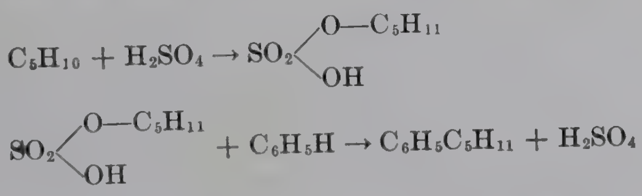
[1] LOHSE, "Catalytic Chemistry," pp. 252–261, 377–383, Chemical Publishing Company of New York, Inc., New York, 1945.

is not understood. Ipatieff calls this eka-catalysis, or unknown catalytic action.

3. Physical catalysis includes a number of those reactions, such as photocatalysis, wherein light or energy other than chemical influences the course of reaction.

Most of the alkylation catalytic reactions come under the classification of reaction multiplier; and in a considerable number of these catalytic alkylations, the unstable intermediate compound with the catalyst is known. In the carbon-to-carbon alkylation of both aromatic and paraffinic hydrocarbons by olefins through the catalytic intervention of sulfuric acid, there is much evidence that the olefin is converted to an alkyl sulfate which then alkylates the other hydrocarbon, the sulfuric acid being regenerated during the process. This is also true of phosphoric acid, and we may postulate these reactions as follows:



$$C_5H_{10} + H_2SO_4 \rightarrow SO_2\left\langle\begin{array}{l} O-C_5H_{11} \\ OH \end{array}\right.$$

$$SO_2\left\langle\begin{array}{l} O-C_5H_{11} \\ OH \end{array}\right. + C_6H_5H \rightarrow C_6H_5C_5H_{11} + H_2SO_4$$

The use of sulfuric acid as a catalyst is discussed under Dimethylaniline (*q.v.*), in the preparation of ethyl ether and of petroleum alkylate. Some technical operations in the vapor phase have been carried on in the presence of a catalyst, and anisole[1] is stated to be formed with very good yield when the vapors of phenol (1 volume) and methanol (1.5 volumes) are conducted over alumina at 390 to 420°C. Hydrogen fluoride is an excellent catalyst for petroleum alkylation.

A technical procedure for the preparation of methylamines is to pass the vapors of ammonia and methanol over aluminum oxide at around 400°C. The pressure is practically atmospheric, and the methanol is used in excess. Mono-, di-, and trimethylamines are obtained.

Effect of Ratio of Reactants.—An excess of the methylating agent acts frequently to better the yield. This is particularly true when the less vigorous alkylating agents, such as the alcohols, are employed in the preparation of dimethyl- or diethylaniline. Use of excess of the alcohol tends to lessen the formation of the monoalkyl derivatives. Diethylation of aniline is more difficult than dimethylation; consequently, the procedure is to separate the monoethylaniline from the diethylaniline by benzylating the monoethylaniline to benzylethylaniline and distilling. In dimethyl sulfate, the first methyl group acts more vigorously than the second; consequently, in difficult alkylations it is better so to proportion the reactants as to use only one of the methyl group. When alkylating with olefins, these are usually diluted with the other reactant such as benzene or isobutane to lessen substantially the polymerizing reaction of the olefin with itself.

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[1] SABATIER and MAILHE, *Compt. rend.*, **151**, 339 (1910).

Alkylations are carried on in alkaline, acid, or neutral media. With dialkyl sulfates, alkali speeds up the reaction (*cf.* Anisole). The vigorous reaction of methyl bromide in alkaline medium is disadvantageous in the methylation of 5-methyl-2-phenylpyrazolone to antipyrine[1] as it leads to trimethylpyrazolones. So here the alkylation is conducted in an acid medium.

In many instances, there is more than one place in the molecule where alkylation can take place. This is true in the methylation of morphine to codeine, where an alcoholic hydroxyl, a phenolic hydroxyl, and a tertiary nitrogen are present. In such cases, it is necessary that only the proper amount of the alkylating agent be used or that special conditions be employed (*cf.* Codeine).

Physical Condition of Alkylating Agent.—The choice of the alkylating agent depends often upon the conditions necessary to handle it, and this sometimes may lead to the use of the less volatile and more expensive alkyl bromide rather than the alkyl chloride. On the other hand, now that dimethyl sulfate and diethyl sulfate are more reasonably priced, they are supplanting the use of the volatile alkyl halides, because, with the sulfates, autoclaves are not so necessary.

Recovery of Alkylated Product.—Wherever possible, rectification furnishes the most convenient and cheapest procedure. This technic is used extensively in the petroleum field. Even in those instances in which the boiling points are rather close together, as is true of the alkyl- and dialkylanilines, a separation can be effected by first benzylating the monoalkyl derivative and then distilling.

The choice of a proper solvent will, in many instances, lead to the crystallization of the alkylated product and to its convenient recovery.

The products from the alkylation of ammonia with methanol are water; mono-, di-, and trimethylamine; and excess methanol. The separation is not easy, but it is carried out by partial condensation to remove excess methanol and water. The vapors are then compressed to several hundred pounds and fractionally distilled under this pressure, yielding some ammonia and the separated amines.

V. EQUIPMENT FOR ALKYLATIONS

Materials of Construction.—Fortunately, steel can be quite generally used even in the presence of the strong acid catalysts, as their corrosive effect is much lessened by the formation of esters as catalytic intermediate products. When hydrogen fluoride is employed, anhydrous conditions prevail, so steel equipment is satisfactory. Enameled liners or completely enameled vessels are available and are increasingly employed; these are quite resistant to acids. In a few cases, copper or tinned copper is still used.

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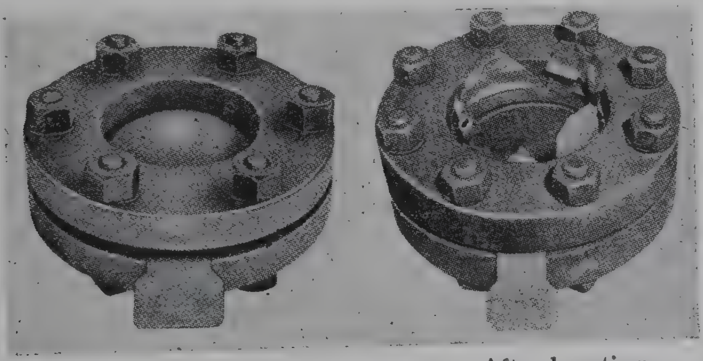
[1] FOURNEAU, "Organic Medicaments and Their Preparation," p. 38, J. & A. Churchill, London, 1925; *cf.* SCHWYZER, *loc. cit.*, pp. 164–169.

Corrosion of Apparatus.—As described later on in the manufacture of dimethylaniline, a steel autoclave is employed even though a small amount of sulfuric acid is used as the catalyst; the large amount of the aniline and dimethylaniline present serves to protect the steel from the action of the acid. The corrosion that takes place is principally localized at the liquid level in the autoclave.

However, there are many cases in which the agents used in alkylation are corrosive. In the alkylation of aniline to diethylaniline by heating aniline and ethyl alcohol, sulfuric acid cannot be used, because it will form ether; consequently, hydrochloric acid is employed, but these conditions are so corrosive that the steel autoclaves used to resist the pressure must be fitted with replaceable enameled liners.



Before bursting After bursting

FIG. 2.—Safety diaphragm (frangible disk) for the relief of excessive autoclave pressures.

Certain other alkylations employing alkyl halides are carried out in an acid condition. For example, hydrobromic acid is formed when methyl bromide is used in the alkylation leading to the manufacture of both antipyrine and pyramidone. For such reactions, an autoclave with a replaceable enameled liner and a lead-coated cover is suitable.

In the manufacture of pharmaceutical and photographic products, great care is necessary to prevent contamination with heavy metals. Here, either tinned iron or tinned copper or an enameled coating is frequently employed. A lead lining is suitable in the kettle for the alkylation leading to metol, N-methyl-*p*-aminophenol sulfate, and, in some instances, the new chromium steel alloys have found favor, as in the reaction of ethyl chloride on ammonia to produce diethylamine.

Type of Equipment.—In many cases of alkylation, autoclaves are necessary. These are generally constructed of steel, with or without an anticorrosion liner. In most instances, it is necessary to heat the autoclave, and this is done, as a rule, through the use of a jacket, although steel autoclaves have been directly heated in a suitably designed furnace using gas flame. When jackets are provided, the most convenient source of heat is direct steam. For higher temperatures, as in the manufacture of dimethylaniline (*q.v.*), superheated steam is used in the jackets of the autoclaves. The circulation of hot oil through the jackets has also been used for supplying the necessary heat. Figure 4, page 598, depicts the type of jacketed autoclave that has been used for the manufacture of dimethylaniline.

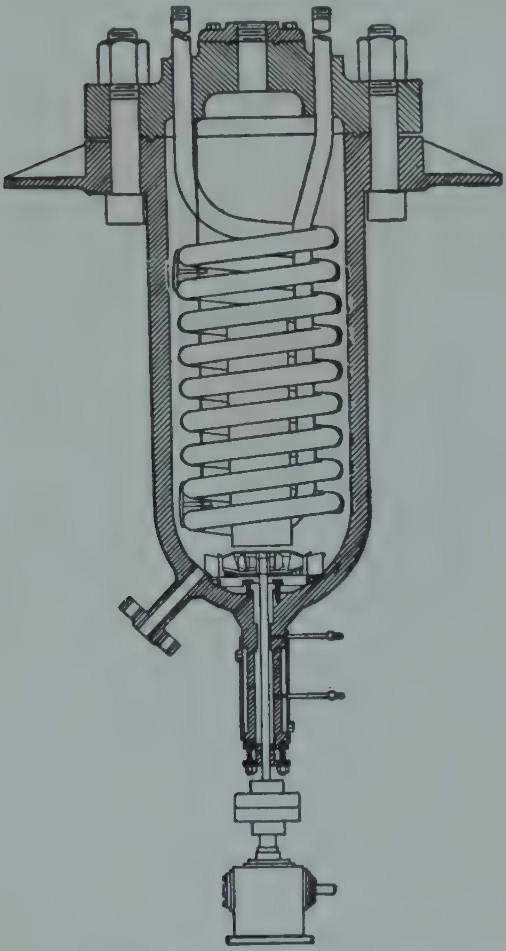


Fig. 3.—Agitated internally heated autoclave. (*Blaw-Knox Company.*)

Naturally, these autoclaves must be provided with inlet and outlet tubes, pressure gauge, thermometer well, and either a safety valve or, better, a safety disk (Fig. 2) that will yield before a dangerous pressure is reached. The safety disk is more certain to function than the safety valve, which may become corroded or clogged. As a rule, it is not necessary to provide a stirring mechanism in the autoclave, in that the heating generally causes sufficient homogeneity, but the contents should always be well stirred before the autoclave is closed and the heating started. Figure 3, however, does show an excellent stirring mechanism for those alkylations where agitation is desired. This figure likewise depicts a cheaper and better method of applying heat or cold by means of an internal coil rather than by a jacket.

By substituting for alkyl halides dimethyl or diethyl sulfate, and in some instances by the use of methyl *p*-toluenesulfonate or even alcohol, it is possible to proceed without the use of an autoclave. A jacketed stirred kettle is generally used, and, in these cases, the operation is carried on at lower temperatures. Such an apparatus is employed in the making of *p*-nitrophenetole from *p*-nitrochlorobenzene by heating with alcoholic potash in the presence of potassium sulfite at 50 to 80°C. (*cf.* Acetophenetidine). Similarly, a lead-lined agitated jacketed kettle is suitable for the methylation of *p*-aminophenol with dimethyl sulfate to furnish metol.

Control of Operation.—To ensure safety, in the control of autoclave procedures, the apparatus should be removed from use for periodic tests or inspection. In most cases, it is sufficient to apply a hydrostatic pressure 50 per cent higher than is used in practice. It is necessary to remove the safety disk or safety valve, as they are usually set to blow at lower than test pressure. Naturally, these instruments and all others must be frequently checked. It is wise to provide not only a mercury thermometer in a well tube but also a recording thermometer.

VI. EFFECT OF ALKYLATION

Although the effect of alkylation on the properties of organic compounds is sometimes contradictory, there are some general observations that are of value, particularly in the field of motor fuels, medicinals, dyes, and solvents.

High-octane motor fuels are manufactured in large amounts by alkylation because suitable branched chains are economically obtained.

Medicinally, this effect has been studied and compiled for numerous compounds and series of compounds. Hartung gives an excellent review of these studies for various aliphatic alkylamines and compounds related to adrenaline, from which the following is quoted:[1]

> The physiological effect of aliphatic amines may be exhibited in various ways. Ammonia in small doses is a respiratory stimulant, but larger doses cause convulsions; it produces a rapid but very transitory depression of the blood pressure. As alkyl groups replace the hydrogen atoms of ammonia, the stimulating action is diminished, becoming less as the size of the alkyl group increases; as the alkyl chain becomes longer, a depressant action on the heart and convulsions of spinal origin appear, the depressant action being perceptible even in isoamylamine.

Schmiedeberg formulated a series of rules regarding the effect of alkyl groups on physiological activity which May summarizes as follows:[2] In the first place, a close connection exists between "medical" action and the ordinary physical properties of volatility and solubility. In the aliphatic paraffin series, the lower members, which are more volatile, exhibit a narcotic effect that is absent in the insoluble, nonvolatile higher members.

Alkylation often causes very poisonous compounds to lose this effect; *e.g.*, the nitriles (RCN) and isonitriles ($\mathrm{R{-}N{\equiv}C}$) are poisonous only when HCN is split off. The action of alkyl radicals can be masked or inhibited by the presence of other radicals; this is illustrated by the behavior of methyl-, dimethyl-, and trimethylamine, which react like ammonia but have no narcotic effect. In this conduct, these amines follow Schmiedeberg's preceding rule and are less toxic than ammonia.

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[1] HARTUNG, *Chem. Rev.*, **9**, 389–465 (1931).

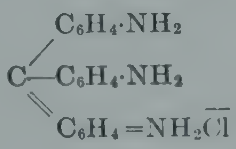
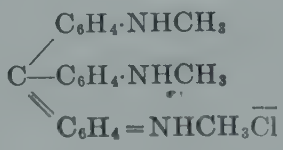
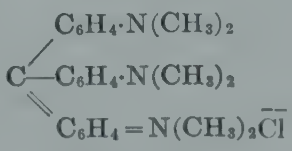
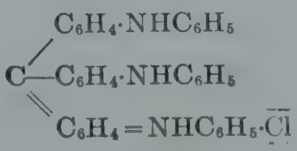
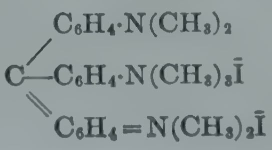
[2] MAY, "The Chemistry of Synthetic Drugs," 3d ed., Longmans, Green and Company, London, 1921.

In the alcohols and the ethers, the physiological action is ascribed to the nature of the alkyl groups. For the ethers, single or mixed, the effect is due to the presence of the alkyls, each of which acts independently of the other.

One of the most interesting studies of the effect of various alkyl groups on physiological activity is illustrated by the alkyl derivatives of resorcinol, which are discussed under Hexylresorcinol. The bactericidal action at first increases with the length of the side chain and then diminishes because of decreased solubility of the alkylresorcinol. Coincident with this increase is found a decrease in toxicity.

Phenol was the first antiseptic used, and a thorough study of its derivatives has been made. The substitution of a methyl group for the hydrogen in the ring of phenol, forming the cresols, increases the antiseptic action. In the case of the dihydroxybenzenes, the alkyl derivatives of resorcinol have been carefully investigated, and it is found that the entrance of the methyl group into the ring, forming orcinol, depresses the bactericidal power. The influence of higher alkyl groups of the nucleus of the resorcinol molecule is considered under Hexylresorcinol (*q.v.*).

COLOR AND CHEMICAL CONSTITUTION

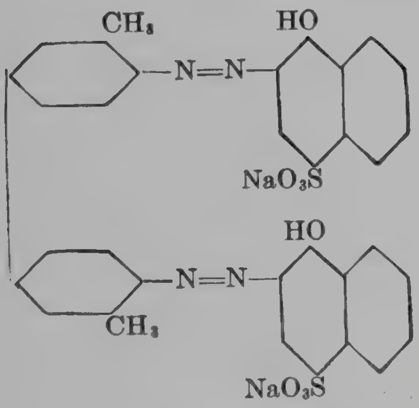
Name	Mol. formula	Mol. wt.	Shade of dyeing
Paramagenta............	 $C\begin{array}{l}\diagup C_6H_4\cdot NH_2\\ -C_6H_4\cdot NH_2\\ \diagdown\!\!\diagdown C_6H_4{=}NH_2\overline{Cl}\end{array}$	281.5	Magenta
Methyl Violet R..........	 $C\begin{array}{l}\diagup C_6H_4\cdot NHCH_3\\ -C_6H_4\cdot NHCH_3\\ \diagdown\!\!\diagdown C_6H_4{=}NHCH_3\overline{Cl}\end{array}$	323.5	Reddish violet
Crystal Violet...........	 $C\begin{array}{l}\diagup C_6H_4\cdot N(CH_3)_2\\ -C_6H_4\cdot N(CH_3)_2\\ \diagdown\!\!\diagdown C_6H_4{=}N(CH_3)_2\overline{Cl}\end{array}$	365.5	Violet
Rosaniline Blue..........	 $C\begin{array}{l}\diagup C_6H_4\cdot NHC_6H_5\\ -C_6H_4\cdot NHC_6H_5\\ \diagdown\!\!\diagdown C_6H_4{=}NHC_6H_5\cdot\overline{Cl}\end{array}$	509.5	Blue
Iodine Green............	 $C\begin{array}{l}\diagup C_6H_4\cdot N(CH_3)_2\\ -C_6H_4\cdot N(CH_3)_3\overline{I}\\ \diagdown\!\!\diagdown C_6H_4{=}N(CH_3)_2\overline{I}\end{array}$	599	Green

In the field of dyes, many observations have been made on the relation of alkylation to the physical properties of these compounds and, in particular, to the color, either visible or as determined by the spectrophotometer. Reference need be made here only to Watson's excellent monograph for the details.[1]

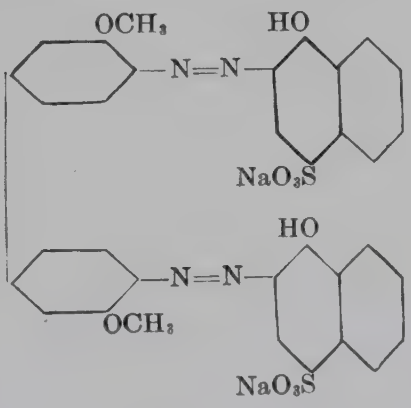
Nietzki early formulated the rule that where the molecular weight of a dye was increased by adding groups to it, a deepening of the color would result. The rule is not of universal application, yet it holds closer for the alkyl radicals and, in particular, when this substitution is effected in the triphenylmethanes.

The table on page 584 (adapted from Watson, *loc. cit.*) is an illustration.

The specific linkage of the alkyl has much influence on any effect that the alkyl group may have on color. When the alkyl is united to carbon in a ring, it does not exert any special influence. However, when the alkyl is combined with oxygen or tertiary nitrogen, the effect on color is marked, the alteration being toward the blue. In the dyes Azo Blue (Colour Index, No. 463) and Benzoazurine (Colour Index, No. 502), there is a change in the former from —CH_3 to —OCH_3, with a color alteration on cotton from reddish violet to a reddish indigo blue.



Azo Blue



Benzoazurine

Among the solvents, a particularly detailed study has been made of the different alkyl derivatives of the glycols, and the tabulation under Cellosolve (*q.v.*) depicts the relationship between the various alkyl ethers of ethylene glycol and certain physical properties of this series.

VII. TECHNICAL ALKYLATIONS

A few selected examples of technical alkylation are here given to illustrate various and typical procedures. These are chosen to illustrate the different linkages and are classified by the type of alkylation linkage.

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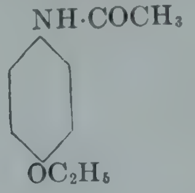
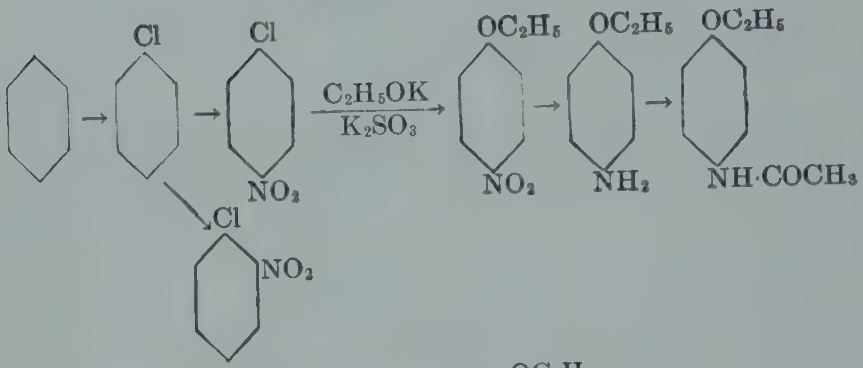
[1] WATSON, "Color in Relation to Chemical Constitution," Longmans, Green and Company, London, 1918.

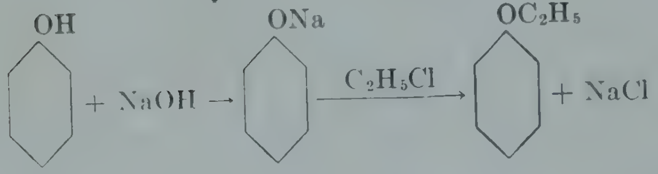
Alkyl Bound to Oxygen.

ACETOPHENETIDINE
PHENACETIN

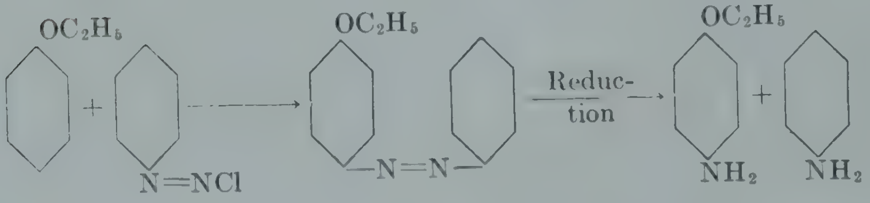

NH·COCH₃
OC₂H₅


Cl
Cl
NO₂
Cl
NO₂
C₂H₅OK
K₂SO₃
OC₂H₅
OC₂H₅
OC₂H₅
NO₂
NH₂
NH·COCH₃

(1)


OH
+ NaOH →
ONa
C₂H₅Cl
OC₂H₅
+ NaCl

(2)


OC₂H₅
+
N=NCl
OC₂H₅
—N=N—
Reduc-tion
OC₂H₅
+
NH₂
NH₂

Acetophenetidine is an important analgesic and antipyretic that has attained widespread use in medicine. The principal series of reactions for its preparation are given above; the one involving the nitration of chlorobenzene is of most value technically. These reactions are intertwined with the preparation of other products; *e.g.*, the orthonitration product of either chlorobenzene or of phenol is methylated to give *o*-nitroanisole, which is made into guaiacol or dianisidine. In general, the alkylation of nitrochlorobenzenes or of the nitrophenols is effected by use of either the alkyl halide or the alcohol—in both cases, in the presence of an alkali. Diethyl sulfate (or dimethyl sulfate) is also employed and can be handled more easily than the alkyl halide.

p-Nitrophenetole from p-Nitrochlorobenzene (Reaction 1).—As Schwyzer points out, *p*-nitrochlorobenzene when heated with alcoholic potash yields but little of the *p*-nitrophenetole.[1] In the presence of sulfites, however, the reaction proceeds smoothly and without the formation of by-products. Potassium sulfite is best, and it should be introduced in powdered form. The temperature also has much effect on the amount of product obtained.

---

[1] Schwyzer, "Die Fabrikation pharmazeutischer und chemisch-technischer Produkte," pp. 211–212, Verlag Julius Springer, Berlin, 1931.

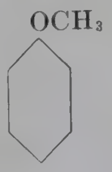
A stirred iron kettle of 1,700 liters capacity, provided with a jacket for hot water, is recommended. One thousand liters of 95 per cent alcohol is introduced into the kettle, and 63 kg. of 94 per cent KOH is dissolved in it at 45°. Five kilograms of powdered potassium sulfite and 157 kg. of *p*-nitrochlorobenzene are then added. The temperature is raised to 50°C., at which point the reaction starts. The charge is maintained at 50°C. for 6 hr., then for 6 hr. at 55°C., and the temperature raised 5°C. at 6-hr. intervals until 80°C. is reached, where the reaction mass should be kept for 12 hr. At each temperature increase, 1 kg. of finely powdered potassium sulfite is added.

The precipitated potassium chloride is put on a pressure filter while still hot, and 7 kg. of potassium sulfite is added to the filtrate, which is returned to the reactor. After 3 hr. at 80°, the filtration is repeated. After this, the transformation is practically complete with almost a theoretical yield. The alcohol is distilled off and can be used again so long as its ethanol content has not dropped below 85 per cent. *p*-Nitrophenetole is isolated from the residuum from the alcohol distillation.

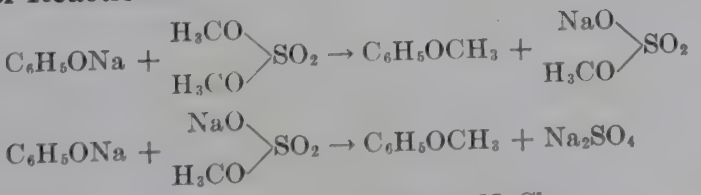
Phenetidine is obtained from *p*-nitrophenetole by reduction with iron and hydrochloric acid. It is then acetylated to *p*-acetophenetidine by heating with glacial acetic acid in a silver-lined still.

p-Phenetidine from p-Ethoxy-azobenzene[1] (Reaction 2).—The Dow Chemical Company's process is based on alkylating sodium phenoxide with ethyl chloride and coupling the alkoxy derivative with diazotized aniline, splitting the *p*-ethoxy-azobenzene by reduction, and recovering aniline—to be used over again—and the *p*-phenetidine. The latter is acetylated to acetphenetidine.

ANISOLE



Outline of Reactions.



$$C_6H_5ONa + \begin{matrix}H_3CO\\ H_3CO\end{matrix}\!>SO_2 \rightarrow C_6H_5OCH_3 + \begin{matrix}NaO\\ H_3CO\end{matrix}\!>SO_2 \qquad (1)$$

$$C_6H_5ONa + \begin{matrix}NaO\\ H_3CO\end{matrix}\!>SO_2 \rightarrow C_6H_5OCH_3 + Na_2SO_4$$

$$C_6H_5ONa + CH_3Cl \rightarrow C_6H_5OCH_3 + NaCl \qquad (2)$$

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[1] BARROWCLIFF and CARR, "Organic Medicinal Chemicals," pp. 116–117, Baillière, Tindall & Cox, London, 1921, describes a more complicated but similar procedure through 4-ethoxy-4′-hydroxyazobenzene.

Anisole is used directly in perfumery and as an intermediate for further synthesis. It is prepared by the action of methyl chloride or of dimethyl sulfate on phenol. When dimethyl sulfate is employed, both of its methyl groups can be made to react, yielding about 72 to 75 per cent of theory of the anisole. When only one of the methyl groups is caused to react, the yield is higher, being from 85 to 95 per cent of theory, but it is usually more economical to use both of the available methyl groups.

Ullmann directs that the reaction be carried out at not higher than 50 or 60°C., treating 9.4 parts of phenol with 50 parts of 10 per cent caustic soda and 12 volume parts of dimethyl sulfate, thus obtaining 10.5 parts of anisole, or 96 per cent of theory.[1] The concentration of the caustic soda does not have much effect upon the yield, but solutions stronger than 10 per cent cause the reaction to go more rapidly. The proportions just given are calculated to leave sodium methyl sulfate in solution. This, however, can be used for alkylation by adding still more phenol and alkali and boiling for rather a long time under a reflux condenser.[2]

The influence of water and time of reaction in the methylation of phenol to anisole are shown in the accompanying table.[3]

TABLE II.—FORMATION OF ANISOLE AT 100°C.
Influence of Water and Time of Reaction

Time, hr.	Dimethyl sulfate, moles	Phenol, moles	Sodium hydroxide, moles	Water, moles	Anisole, %
1	0.1	0.2	0.3	0.0	54.5
1	0.1	0.2	0.3	0.2	70.0
1	0.1	0.2	0.3	0.4	64.5
1	0.1	0.2	0.3	0.8	61.8
1	0.1	0.2	0.3	1.6	54.6
1	0.1	0.2	0.3	3.2	39.3
5	0.1	0.2	0.3	0.2	90.1
5	0.1	0.2	0.3	0.4	81.2

From the data in Table II, the authors conclude that the first methyl group in dimethyl sulfate reacts rapidly to form anisole and that the second methyl group reacts slowly, particularly in the presence of a relatively large amount of water. If the water concentration is reduced and sufficient time is allowed, the second methyl group may be largely used.

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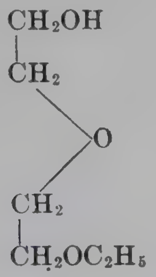
[1] ULLMANN, "Enzyklopädie der technischen Chemie," Zte. Auflage, I, 239, Urben & Schwartenberg, Berlin, 1928–1932.

[2] ULLMANN and WENNER, *Ber.*, **33**, 2476 (1901); ULLMANN, *Ann.*, **327**, 114 (1930); GRAEBE, *Ann.*, **340**, 208 (1905); GILMAN, "Organic Synthesis," Collective Vol. **I**, p. 50, John Wiley & Sons, Inc., 1932.

[3] LEWIS, SHAFFER, TRIESCHMANN, and COGAN, *Ind. Eng. Chem.*, **22**, 34 (1930).

CARBITOL

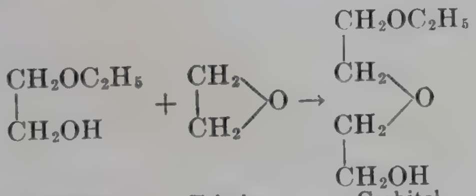
DIETHYLENE GLYCOL MONOETHYL ETHER
2-(β-ETHOXYETHOXY)ETHANOL



Polyethylene glycols as high as the octaethylene glycol have been prepared.[1] The ethers of these polyethylene glycols have attained commercial significance, and this is particularly true of the diethylene glycol ethyl ether, which is sold commercially under the name of Carbitol. This product is especially useful in the manufacture of laminated glass, wherein the celluloid interleaf is misted over with a spray of Carbitol, which increases the adhesion to the glass. In the printing and dyeing of textile fabrics, it makes possible more economical use of dyes.

Carbitol is a solvent with a mild odor and a low rate of evaporation, with a boiling point of 201.9°C. It enters into the manufacture of wood stains and automobile polishes and is used as a lacquer solvent. However, it is particularly valuable in the cosmetic field, where it is employed for creams and hair tonics.

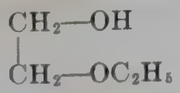
Preparation.—The diethylene glycol monoethyl ether is prepared by the condensation of Cellosolve (see below) with ethylene oxide and, as would be expected, is obtained as a by-product in the preparation of the ethylene glycol ethyl ether.



Cellosolve Ethylene Oxide Carbitol

CELLOSOLVE

ETHYLENE GLYCOL ETHYL ETHER
2-ETHOXYETHANOL



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OC_2H_5 \end{array}$$

Ethylene glycol ethyl ether belongs to three major chemical families: it contains an alcoholic group, —OH; a hydrocarbon group, $\overset{|}{C}H_2\cdot\overset{|}{C}H_2$;

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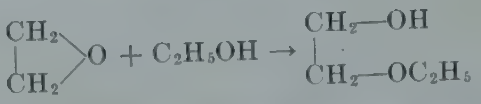
[1] LAWRIE, "Glycerol and Glycols," pp. 381 *et seq.*, Reinhold Publishing Corporation, New York, 1928.

and an ether group, $—CH_2—OC_2H_5$, and it is not surprising that this compound and its homologues have proved to be useful solvents.

Since the ethylene glycol ethers contain an ether as well as an alcohol group, they are very good solvents for cellulose esters. The ethylene glycol methyl ether is an excellent solvent for both nitro- and acetylcellulose, whereas the ethyl and the higher homologous ethers dissolve only the nitrocellulose.

Because of the strong solvent action of the methyl ether of ethylene glycol, the so-called Methyl Cellosolve, it is used to seal the Cellophane-covered cigarette packages. Here, only 6 drops are needed per package, and yet Methyl Cellosolve is sold in carload quantities.

Preparation.



Absolute ethyl alcohol is conducted into an autoclave, and ethylene oxide[1] as a liquid under pressure is introduced in such a quantity as to leave the alcohol in 15 per cent excess. The autoclave is closed, and the temperature raised to 150°C. for 12 hr. or 200°C. for 4 hr. At 150°, the pressure mounts to 250 lb. at the start of the reaction, falling toward the end to 125 lb. The autoclave is discharged, and the product fractionally distilled. After the removal of the excess alcohol, the ethylene glycol ethyl ether passes over at around 134°C. A yield of about 70 per cent, based upon the alcohol consumed, is obtained. In the still are the higher boiling reaction products, such as the ethyl ethers of di- and triethylene glycol. The excess alcohol presumably diminishes the amount of these by-products.

Other reactions are available whereby these glycol ethers can be formed. According to one patent, ethylene glycol, diethyl sulfate, and caustic soda, in the quantities required by the equation below, are boiled for 3 hr. in a kettle under a reflux.[2]

$$2HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH + 2NaOH + (C_2H_5)_2SO_4 \rightarrow 2HO{\cdot}CH_2{\cdot}CH_2OC_2H_5 + Na_2SO_4 + 2H_2O$$

The products are rectified by distillation, leaving the inorganic matter in the still. The yield is 60 per cent or over. Ethylene oxide[3] has been reacted with ethyl alcohol under the influence of heat and pressure and a small quantity of diethyl sulfate, to form ethylene glycol ethyl ether. The ethylene oxide and alcohol reaction has also been catalyzed by boiling with special hydrosilicates.[4] In another process, these ethers are formed from ethylene chlorohydrin, a slight excess of diethyl sulfate and solid caustic soda by boiling under a reflux condenser for 3 hr.[1] The yield is 60 per cent or greater.

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[1] U. S. 1,696,874 (1928).

[2] U. S. 1,614,883 (1927).

[3] Birch and Scott, U. S. 1,882,564 (1932); Ger. 580,075.

[4] Ger. 558,646.

$$2HOCH_2\cdot CH_2Cl + 4NaOH + (C_2H_5)_2SO_4 \rightarrow 2CH_2OH\cdot CH_2O\cdot C_2H_5 + Na_2SO_4 + 2NaCl + 2H_2O$$

In the foregoing reactions, various alcohols can be used as alkylating agents, even those containing an aromatic group, but the principal ones that have found favor are methyl, ethyl, and butyl alcohols. As a rule, the diethers have little or no advantage over the monoethers, the alcohol-ether compound giving the most desirable properties. The data in Table III permit a comparison of some of the physical properties of these ethers and show the influence of different alkyl groups upon the boiling point, specific gravity, and refractive index of this series.

TABLE III.—BOILING POINTS, SPECIFIC GRAVITY, AND REFRACTIVE INDICES OF ETHYLENE GLYCOL ETHERS[1]

Monoalkyl ether	B.p.,[2] °C.	Sp. gr., 15°C./15°C.	Refractive index (η_D) at 26°C.
Methyl	124.3	0.9748	1.4004
Ethyl	135.1	0.9360	1.4042[3]
Isopropyl	144.0	0.9139	1.4080
n-Propyl	150.0	0.9110	1.4125
Isobutyl	158.8	0.9130	1.4135
n-Butyl	170.7	0.9188	1.4177
Isoamyl	181.0	0.9000	1.4198

[1] Lawrie, *op. cit.*

[2] 743 mm. pressure.

[3] 24°C.

ETHYLCELLULOSE

The cellulose ethers obtained by the alkylation of cellulose are important plastic materials. They are more stable than the cellulose esters and are incapable of undergoing hydrolysis, which makes them more resistant to acid and alkalies. The alkyl ethers are, however, soluble to a considerable extent in water and alkalies, more so than benzyl cellulose but less than cellulose acetate.

The data below show how the solubility of the alkyl ethers varies with the percentage of etherification.[2]

Ether	Soluble in alkali	Soluble in water	Soluble in organic solvents
Methyl cellulose	3–4 % —OCH_3	22–26 % —OCH_3	40 % —OCH_3
Ethyl cellulose	5 % —OC_2H_5	27 % —OC_2H_5	47 % —OC_2H_5

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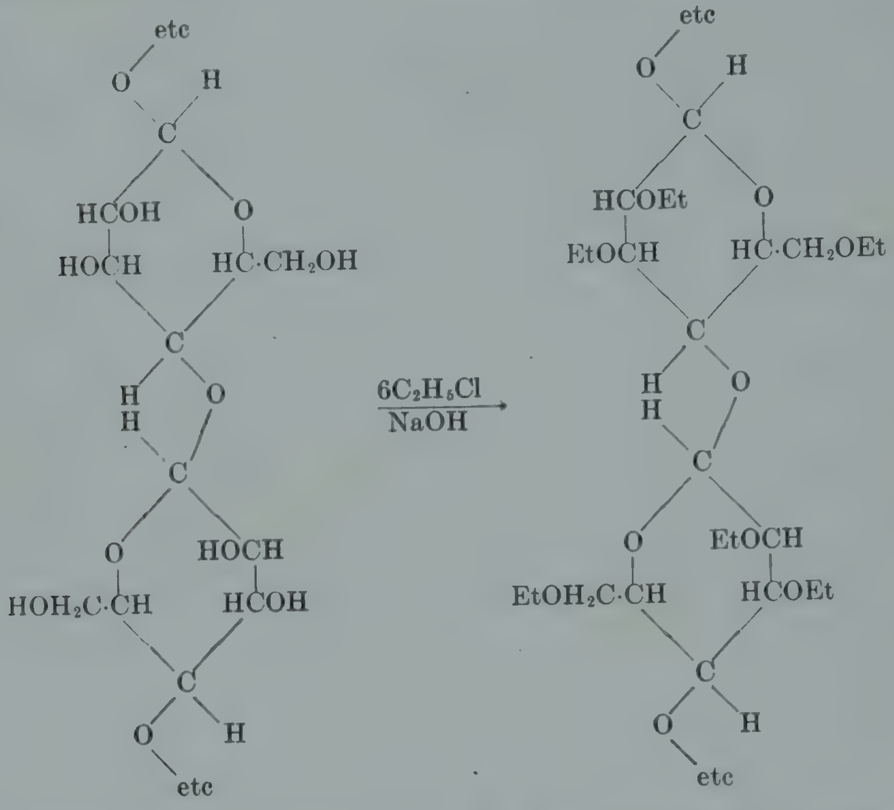
[1] U. S. 1,732,356 (1929).

[2] TRAILL, *Oil and Colour Trades J.*, pp. 1109 (1936).

The alkali-soluble compounds are of interest to the textile industry but are not suitable for the preparation of lacquers. Of the ethylcellulose now manufactured, about 70 per cent is consumed as plastics while about 30 per cent is compounded into protective coatings.



Preparation.—The manufacture of ethylcellulose by the Hercules Powder Company is carried out as follows:[1]

The purified cellulose (sheeted chemical cotton or sulfite pulp) is shredded and introduced into a covered, horizontal monel metal trough where it is "wetted" with iron-free caustic soda solution and conveyed to the reactors or alkylators. These alkylators are steam-jacketed autoclaves of 4500-gal. capacity, tested to 700 lb. per sq. in., constructed of nickel-clad steel, and provided with solid nickel shafts and agitators. The alkylator is charged with the alkali cellulose and with ethyl chloride, and the temperature raised to nearly 205°, resulting in the formation of ethylcellulose, salt, ether, and alcohol. For every 100 lb. of cellulose charged, 125 lb. of ethylcellulose is produced. The ethoxy content and the viscosity are governed by operational variables such as time, temperature, pressure, and selection of raw materials.

At the end of the processing cycle in the alkylator, the ether and alcohol formed are flashed off and washed with sulfuric acid in lead scrubbing equipment to remove harmful low-boiling contaminants. The solvents are condensed and then carefully rectified in copper columns to separate minor volumes of unreacted ethyl chloride from the ether and the alcohol. The latter two are separately reconverted to ethyl chloride using hydrochloric acid manufactured at the plant from salt and sulfuric acid in a large Laury-type furnace and Karbate and Haveg condensation equipment.

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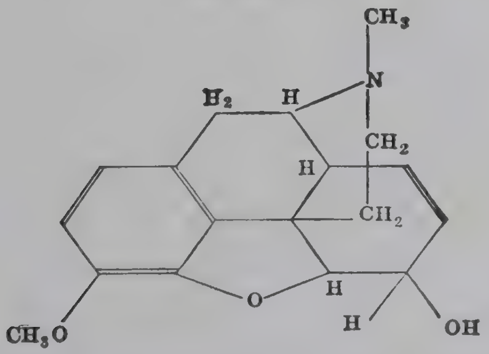
[1] Anon., *Chem. Met. Eng.*, **52**, No. 9, 129–141 (1945), with pictured flow sheet.

The ethylcellulose precipitates in the alkylator when the solvents are distilled off as a slurry in a weak caustic solution saturated with salt. The rather large granules of ethylcellulose are transferred to a disintegrator, then to a nickel screen for separation and washing. The product is specially purified, centrifuged, dried, and packed for shipment. The weak caustic and saturated salt solution is evaporated in a double-effect nickel-clad Zaremba evaporator, separated, and centrifuged in a Bird centrifuge, and both caustic and salt are reused.

The resulting ethylcellulose is a powdery flocculent substance which is soluble in a number of organic solvents (*e.g.*, chloroform, alcohol, chloroform-alcohol mixture, chloroform-methyl alcohol mixture, glacial acetic acid, amyl acetate, and nitromethane), and these solutions give clear, transparent, flexible, and water-resistant films when evaporated.

The aralkyl celluloses, *e.g.*, benzyl cellulose and phenylethyl cellulose, are made in a similar manner. Their purification may be accomplished by treating the crude alkylation mass with a selective solvent, *e.g.*, propanol or diamyl ether, which removes organic impurities.[1] The granular precipitate is then washed with methanol and finally with water.

CODEINE



Codeine ($CH_3O(C_{17}H_{17}ON)OH$) occurs naturally in opium and is extracted industrially along with morphine. It is derived from morphine ($HO(C_{17}H_{17}ON)OH$) by methylation of the phenolic hydroxyl. Because the demand for codeine for many years has exceeded the quantities that were available by natural extraction from opium, a great deal of work has been done on the synthesis of codeine from morphine.[2]

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[1] U. S. 2,101,032 (1937).

[2] SMALL, "Chemistry of the Opium Alkaloids," Supplement 103 to Public Health

In this and similar methylations, it is particularly difficult to secure the excellent yields that are necessary for the economic handling of such high-priced materials. In the morphine and codeine molecules, a tertiary nitrogen is present that can be alkylated to a "pentavalent" condition by the simple addition of methyl iodide or similar alkylating agents, whereupon the ring system is quite liable to be destroyed, following the reaction known as Hofmann's exhaustive methylation. Consequently, the treatment of morphine with the ordinary simple methylating compounds results in low yields of codeine and considerable destruction of the molecule. This applies to the treatment of the anhydrous solution of sodium morphinate with the ordinary alkylating agents, such as a methyl halide or dimethyl sulfate.[1]

On the other hand, as has been described by Boehringer,[2] Rodionov,[3] Schwyzer,[4] and Small,[5] high yields are obtained if a quaternary methylating agent is employed. With a quaternary ammonium base having nitrogen in the pentavalent condition, there is little or no tendency to form a pentavalent nitrogen derivative on the morphine nitrogen with consequent destruction of the morphine-ring system. Hence, the methylation proceeds almost exclusively on the phenolic hydroxyl, resulting in excellent yields of the methyl ether, codeine.

Methylation Reactions with Quaternary Nitrogen Methyl Derivatives.[6]

$$C_6H_5N(CH_3)_2 + CH_3Cl \rightarrow C_6H_5N(CH_3)_3Cl \qquad (1)$$

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$$

$$\underset{\text{Morphine}}{HO(C_{17}H_{17}ON)OH} + \underset{\text{Phenyltrimethylammonium Chloride}}{C_6H_5N(CH_3)_3Cl} + \underset{\text{Sodium Ethylate}}{C_2H_5ONa} \rightarrow$$

$$\underset{\text{Codeine}}{CH_3O(C_{17}H_{17}ON)OH} + \underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} + \underset{\text{Ethanol}}{C_2H_5OH} + NaC$$

$$C_6H_5SO_3H + ClSO_2OH \rightarrow C_6H_5SO_2Cl + H_2SO_4 \qquad (2$$

$$C_6H_5SO_2Cl + CH_3OH + NaOH \rightarrow C_6H_5SO_2OCH_3 + NaCl + H_2O$$

$$C_6H_5SO_2OCH_3 + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_3OSO_2C_6H_5$$

$$C_6H_5N(CH_3)_3OSO_2C_6H_5 + NaOH \rightarrow C_6H_5N(CH_3)_3OH + NaOSO_2C_6H_5$$

$$C_6H_5N(CH_3)_3OH + HO(C_{17}H_{17}ON)OH \rightarrow$$

$$CH_3O(C_{17}H_{17}ON)OH + C_6H_5N(CH_3)_2 + H_2$$

$$p\text{-}CH_3C_6H_4SO_2OCH_3 + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_3OSO_2C_6H_4CH_3 \qquad (3$$

$$HO(C_{17}H_{17}ON)OH + C_6H_5N(CH_3)_3OSO_2C_6H_4CH_3 + C_2H_5ONa \rightarrow$$

$$CH_3O(C_{17}H_{17}ON)OH + C_6H_5N(CH_3)_2 + NaOSO_2C_6H_4CH_3 + C_2H_5O$$

Reports, pp. 147, 175–176, 188, U. S. Government Printing Office, Washington, D. C (1932).

[1] Barrowcliff and Carr, *loc. cit.*, pp. 55–57.

[2] Boehringer and Söhne, Ger. 247,180 (1909).

[3] Rodionov, *Bull. soc. chim.*, **39**, 305–325 (1926); **45**, 109–121 (1928).

[4] Schwyzer, *loc. cit.*, pp. 374, 388–392.

[5] *Loc. cit.*

[6] It is clear that the formation of phenyltrimethylammonium chloride exemplifie alkyl bound to pentavalent nitrogen.

Methylation According to Reaction (1).—Phenyltrimethylammonium chloride is an excellent methylating compound not only for morphine but for a number of other compounds such as antipyrine and theobromine. It is prepared and used according to the method of Schwyzer by warming dimethylaniline with methyl chloride in a 100-liter stirred autoclave provided with an enameled liner.[1] Into this autoclave are charged 10 kg. of dimethylaniline, 4 kg. of absolute alcohol, and 4.5 kg. of methyl chloride. The autoclave is closed and heated gradually to 100 to 120°C., whereupon the pressure rises to about 400 lb., chiefly owing to the presence of the excess of methyl chloride. The stirrer is run one-half day, and, as the reaction progresses, the pressure drops. The autoclave is allowed to cool and is opened the following morning. The crystals are filtered off, dried immediately at 50 to 60°C., and then transferred while still warm into closed containers. These crystals are very hygroscopic. The yield amounts to 12.5 to 13 kg. The sodium ethylate is prepared by dissolving metallic sodium in absolute alcohol. Schwyzer directs that 96 per cent alcohol be used, but other workers prefer absolute alcohol.

When this methylating compound is used, it is necessary to conduct the operation in an autoclave which should be charged with 10 kg. of anhydrous morphine alkaloid, 7 kg. of absolute alcohol, and 14.1 liters of sodium ethylate solution of such strength that 25 cc. will neutralize 60 cc. normal hydrochloric acid. The autoclave contents are carefully mixed, 6.5 kg. of phenyltrimethylammonium chloride are then introduced, and the autoclave is closed and slowly warmed to a pressure of 60 lb. The vapors are blown off, and the autoclave allowed to cool overnight.

The contents of the autoclave are dissolved in 20 liters of water, and the alcohol distilled off, after which the product is made acid to litmus with dilute sulfuric acid, 60 liters of water added, and the dimethylaniline distilled off. Codeine is separated from the small amount of unaltered morphine by extraction with 40 liters of benzene after making alkaline with caustic soda. The benzene-codeine extraction is repeated twice. About 500 to 700 gm. of unaltered morphine can be recovered by acidifying the alkaline aqueous liquor and adding ammonia. Codeine is obtained usually by treating the benzene extracts with 40 liters of 1:10 sulfuric acid. The yield is 91 to 93 per cent.

Methylation According to Reactions (2) *and* (3).[2]—These methods depend on the preparation of an alcoholic solution of the phenyltrimethylammonium hydroxide directly [reaction (2)] or indirectly [reaction (3)] with the sodium salt either of the benzenesulfonate or of the toluenesulfonate being thrown out of solution. The alcoholic solution of the alkylating agent is then reacted with the compound to be methylated.

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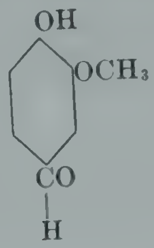
[1] Schwyzer, *loc. cit.*, pp. 388–390.

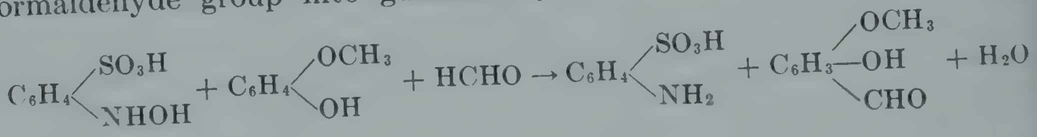
[2] See 2nd edition of this book for details on Rodionov and Small, *op. cit.*

VANILLIN
3-METHOXY-4-HYDROXYBENZALDEHYDE



The chemical transformation of a closely related, naturally occurring product into vanillin has long been the important source of supply. Among such available materials, oil of cloves is used most extensively, the eugenol being converted into isoeugenol and then into vanillin. In this case, the methoxy group found in vanillin is present in the original eugenol. Vanillin is also being made on a large scale by caustic soda treatment of lignin.

A great amount of work has been done on the synthesis of vanillin from cheap organic compounds. Several processes have been made to compete, probably the most important being that which introduces the formaldehyde group into guaiacol by the reaction of guaiacol[1] with formaldehyde and phenylhydroxylaminesulfonic acid.



$$C_6H_4\left\langle\begin{matrix}SO_3H\\NHOH\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}OCH_3\\OH\end{matrix}\right. + HCHO \rightarrow C_6H_4\left\langle\begin{matrix}SO_3H\\NH_2\end{matrix}\right. + C_6H_3\left\langle\begin{matrix}OCH_3\\OH\\CHO\end{matrix}\right. + H_2O$$

Alkyl Bound to Trivalent Nitrogen.

DIETHYLAMINE

$(C_2H_5)_2NH$

Diethylamine finds extensive use in the preparation of wetting and dispersing agents and enters into many syntheses. Through its employment, the alkyl groups are introduced into procaine. Its preparation from ethanol and ammonia by ammonolysis is described in Chap. VI. Here the synthesis from ethyl chloride and ammonia as given by Schwyzer is presented.[2]

$$2C_2H_5Cl + 3NH_3 \rightarrow 2NH_4Cl + NH(C_2H_5)_2$$

A 500-liter autoclave made of corrosion-resisting steel tested to 900 lb. and provided with a jacket for heating and cooling may be employed. Fifty kilograms of absolute alcohol is introduced into the autoclave, and cooled by brine to −15°C., and 10 kg. of ammonia is added. Twenty-six kilograms of pure ethyl chloride and, as a catalyst, 100 gm. of powdered pyrolusite are then introduced.

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[1] Fr. 283,920 (1899); Ger. 105,798 (1900).

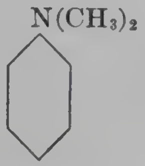
[2] Schwyzer, *op. cit.*, pp. 230–233.

The autoclave is warmed with the use of steam, the procedure being conducted very carefully and slowly. A pressure of 150 to 225 lb. will be obtained if the reaction is kept under control; otherwise, this will mount much higher. Toward the end of the reaction, the pressure will drop, and the temperature should then be raised to 95 to 100°C. When the pressure remains constant at the same temperature, the reaction is completed. The reaction mixture is cooled to 0°C., and the product passed through a closed filter into the rectification apparatus. This reaction mixture contains the following, besides ammonium chloride and a trace of ethyl chloride:

Products	B.p., °C.
$C_2H_5NH_2$	18
$(C_2H_5)_2NH$	56
C_2H_5OH	80
$(C_2H_5)_3N$	89

These products can be separated by fractionation, the yield being between 7 and 10 kg. of diethylamine. The ethylamine should be added to the next run. The triethylamine can be sold as such or used to make ethyl chloride and diethylamine by heating the triethylamine hydrochloride.

DIMETHYLANILINE



Dimethylaniline is very widely used as an intermediate in the manufacture of dyes, rubber accelerators, explosives, and some medical products. Such important dyes as Auramine, Malachite Green, Methyl Violet, Crystal Violet, and Methylene Blue are derived from dimethylaniline. This compound also finds application in the preparation of quaternary alkylating compounds, such as are described under Codeine. The explosive tetryl, which is trinitrophenylmethylnitramine, is manufactured by the nitration of dimethylaniline.

The present technical preparation of dimethylaniline depends upon heating aniline, methanol, and an acid in an autoclave.

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$

Although the literature states that either hydrochloric or sulfuric acid can be used, technically only the sulfuric is employed, as the hydrochloric acid is too corrosive.

The technical preparation of dimethylaniline proceeds along these lines: 200 lb. of aniline is mixed with 220 lb. of methanol, and 20 lb. of 66°Bé. sulfuric acid is added. The mixture becomes warm, and considerable aniline sulfate separates out; this is well stirred and then pumped into a steel autoclave of sufficient capacity to allow for expansion of the charge when hot. The autoclave is heated during the course of 2 hr. to around 205°C. and then maintained at 205°C. or slightly higher for 5 or 6 hr., the pressure rising to around 525 lb. or sometimes 550 lb. The autoclave either can be allowed to cool or can be discharged while still hot, through a cooling condenser into a neutralizing vessel. Here the acid is neutralized with caustic soda, after which the products of the reaction are subjected to vacuum distillation for the recovery of the excess methanol and the purification of the dimethylaniline produced. A yield of around 95 per cent, based on aniline used, is obtained; the net yield, based on the methanol, is somewhat smaller. When the reaction is carried to completion, the dimethylaniline should not contain more than 0.4 per cent of monomethylaniline.

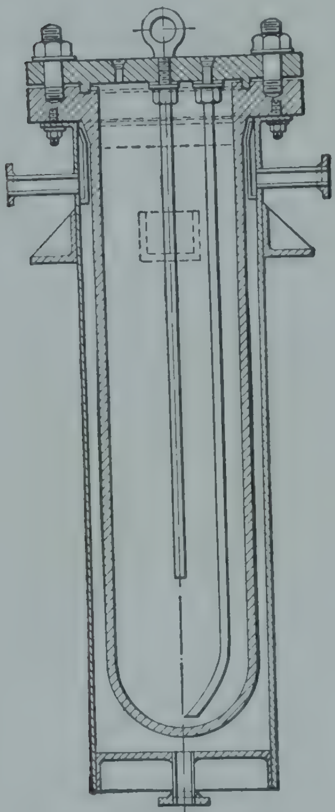
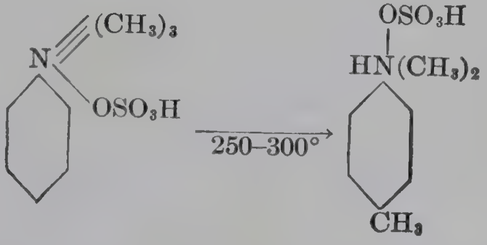


FIG. 4.—Autoclave.

An unlined steel autoclave can be used very satisfactorily for this purpose (see Fig. 4), although periodic hydraulic tests should be made on the apparatus at 500 lb. in excess of working pressure, to ensure its continued safe condition. An occasional inspection should be made, at least of the upper section at the vapor line where corrosion is most likely to occur. Various heating mediums have been employed, such as direct fire, circulated hot oil, or superheated steam. For the last, which is certainly the cleanest and most convenient heating medium, 200 to 250°F. superheat should be given to the ordinary steam at 100 lb. pressure.

It is necessary that dimethylaniline be free from all except a few tenths of 1 per cent of monomethylaniline; consequently, great care must be taken in conducting the initial reaction, as monomethylaniline is difficult to separate by distillation because of the small boiling-point difference between the two. Benzylation of the monomethylaniline yields benzylmethylaniline, and this derivative can be separated easily from the dimethylaniline by fractionation. The formation of similar derivatives of monomethylaniline with toluenesulfonyl chloride or with phthalic acid[1] removes this by-product more completely.

In this methylation, a number of side reactions occur to a small extent. The quaternary ammonium salt $[C_6H_5N(CH_3)_3 \cdot HSO_4]$ is formed and is quite stable, being decomposed by heating with concentrated caustic soda only when the temperature is elevated considerably (170 to 180°C.). There are some nuclear methylated products which are very probably formed from the quaternary compound. Nuclear methylation is more pronounced at temperatures of around 250°C. and is one of the reasons for avoiding such high temperatures or local overheating. In case the reaction does not go to completion, the heating period rather than the temperature should be increased. Excessive sulfuric acid also appears to lead to formation of nuclear products. Nuclear methylation can be carried far enough, for example, by heating under pressure at a temperature of 300 to 350°C., to form mesidine (2, 4, 6-trimethylaniline) as well as *p*- and *o*-toluidine, *m*-xylidine, etc. However, it is unlikely that the conditions in the manufacture of dimethylaniline ever go beyond the following reaction:



In the technical manufacture of dimethylaniline, the formation of some substituted diphenylmethanes is observed. Here, undoubtedly part of the methyl alcohol is oxidized to formaldehyde, causing this condensation. Much of the loss of methanol is due to the formation of methyl ether, which is usually lost in the blowoff at the end of the run.

Alkyl Bound to Pentavalent Nitrogen.

PHENYLTRIMETHYLAMMONIUM CHLORIDE

This product is described under Codeine.

Alkyl Bound to Carbon.

ALKYLATE FOR PETROLEUM INDUSTRY[2]

Direct alkylation of paraffins by olefin hydrocarbons was one of the most important unit-process developments of recent years in the petroleum industry and was the basis for the plants producing high-quality blending stocks or alkylates for wartime high-octane aviation fuels. This unit process has been brought to successful commercial operation based on both thermal and catalytic reactions.

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[1] Britton and Holmes, U. S. 1,890,246 (1932).

[2] Particular acknowledgment is made to the Phillips Petroleum Company for much help in this section on petroleum alkylation.

Essential conditions that have been adopted, as mentioned under Ratio of Reactants, to favor the paraffin-olefin alkylation reaction are the maintenance of a low olefin concentration, which suppresses the tendency of these hydrocarbons to polymerize, and of a high paraffin concentration to favor the paraffin-olefin junction. From a thermodynamic point of view, low temperatures and high pressures displace the equilibrium in favor of the alkylation reaction.[1] The above factors are applied both in the thermal alkylation and also in the catalytic-alkylation processes.[2,3,4] Catalysts permit the use of low temperatures and pressures and require the consideration of their specific behavior in arriving at optimum conditions. The most important catalysts in industrial use for this process are sulfuric acid, hydrogen fluoride, and aluminum chloride-hydrocarbon complex.

Aromatic alkylation with olefins, producing cumene (isopropylbenzene) or ethylbenzene, has been of fundamental help in making, respectively, high-octane gasoline or styrene for rubber.

Thermal Alkylation.—A commercial-scale thermal alkylation unit operated by the Phillips Petroleum Company at Borger, Tex., has alkylated both isobutane and normal butane with ethylene:

$$C_4H_{10} + C_2H_4 \rightarrow C_6H_{14}$$

In the process using isobutane, the major hydrocarbon present in the product is 2, 2-dimethylbutane (neohexane) which has an octane number of 95 and is useful for aviation fuels (see Table IV, page 603).

The operation of the plant is shown in Fig. 5. Ethylene is obtained by cracking a mixture of propane and ethane at 760°C. (1400°F.) and a few pounds per square inch. The ethylene is then absorbed up to about 30 mole per cent in liquid isobutane which has been cooled to about −35° (−30°F.), hydrogen and methane escaping in the gas phase. In the alkylation operation, the isobutane feed to the unit is preheated in a furnace to about 510°C. (950°F.) at about 4500 lb. per sq. in. It is conducted through the alkylation furnace where the olefin feed (ethylene-isobutane mixture) is multipoint injected at 16 places along the line of flow. In this way, the olefin concentration is kept low and the isobutane concentration high in order to favor alkylation. The average mole ratio of isobutane to olefin in the alkylation zone is about 15:1.

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[1] SACHANEN, "Conversion of Petroleum," Reinhold Publishing Corporation, New York, 1940.

[2] Frey, U. S. 2,002,394 (1935).

[3] FREY and HEPP, *Ind. Eng. Chem.*, **28**, 1439 (1936).

[4] OBERFELL and FREY, *Oil Gas J.*, **38**, No. 28; **50**, No. 29, 70 (1939).

The reaction mixture is cooled and fractionated to remove (1) propane and lighter in a depropanizer; (2) isobutane in a debutanizer; (3) heptanes and heavier; and (4) pentanes in a depentanizer. The final products are pentane, neohexane, and motor fuel. Propane is recycled to the cracking step, and isobutane to the alkylation step. Neohexane can be used as a valuable ingredient for aviation fuels, and the heavier hydrocarbons constitute a high-grade motor fuel.

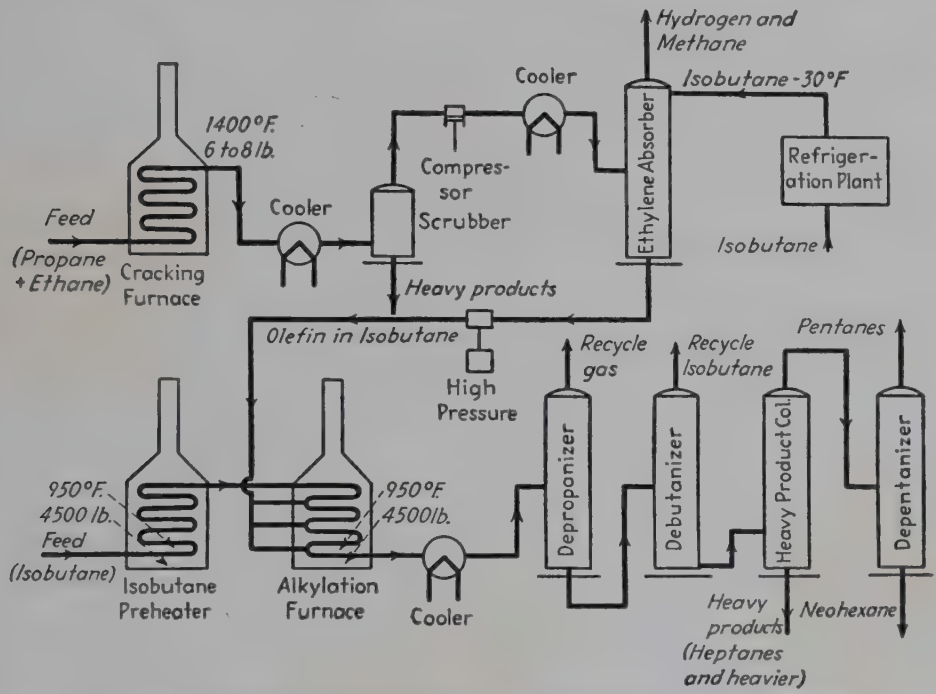
Hydrogen and Methane
Cooler
Isobutane -30°F
1400°F. 6 to 8 lb.
Ethylene Absorber
Compressor
Refrigeration Plant
Feed
Cooler
Scrubber
Isobutane
(Propane + Ethane)
Cracking Furnace
Heavy products
Olefin in Isobutane
Pentanes
Recycle gas
Recycle Isobutane
High Pressure
950°F. 4500 lb.
Feed (Isobutane)
Depropanizer
Debutanizer
Heavy Product Col.
Depentanizer
950°F 4500 lb.
Isobutane Preheater
Alkylation Furnace
Cooler
Heavy products (Heptanes and heavier)
Neohexane

FIG. 5.—Thermal alkylation process. (*Phillips Petroleum Company.*)

Other hydrocarbons can be alkylated under similar conditions. Ethylene is the most active olefin in the thermal process, followed by propylene, *n*-butylenes, and isobutylene in order of decreasing activity. Normal or isoparaffins may be alkylated with equal ease; pentanes, butanes, and propane react readily.

Table IV shows the major hydrocarbons formed by thermal alkylation of various paraffins with ethylene or propylene.[1] Other competing reactions can take place simultaneously: for example, polymerization of the ethylene to butylenes or higher olefins; dehydrogenation and cracking of the paraffin; alkylation with the olefins formed in these reactions; and isomerization, disproportionation, or further alkylation of the primary alkylate. The extent of these secondary reactions varies with operating conditions, the alkylate containing 35 to 75 per cent of the major hydrocarbons, (see Tables IV–VI).

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[1] Phillips Petroleum Company.

Typical operating conditions and yields for thermal alkylation are given in Table VII. There is considerable flexibility in operating conditions, and the yields vary considerably with such changes as well as with feed variations. The inclusion of substantial amounts of olefins other than ethylene affects both the character and the yield of alkylate.

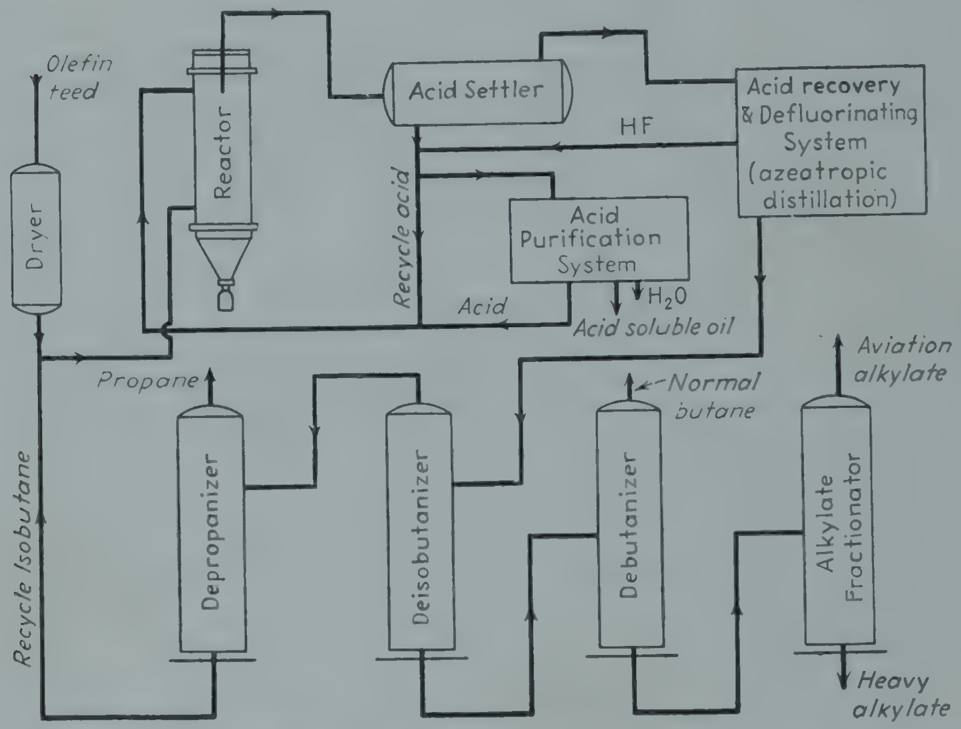
Olefin feed
Dryer
Reactor
Acid Settler
HF
Acid recovery & Defluorinating System (azeotropic distillation)
Recycle acid
Acid Purification System
H_2O
Acid
Acid soluble oil
Propane
Recycle Isobutane
Depropanizer
Deisobutanizer
Normal butane
Debutanizer
Aviation alkylate
Alkylate Fractionator
Heavy alkylate

FIG. 6.—Simplified flow diagram: HF alkylation process. (*Phillips Petroleum Company.*)

HF Alkylation.—The development of catalysts for carrying out the paraffin-olefin alkylation process has permitted lower temperatures and pressures to be employed. One of the most versatile catalysts for this process is hydrogen fluoride. This process was under development prior to the outbreak of war but was brought to a commercial scale mainly during the period after 1941.

The process differs from thermal alkylation in that it takes place in the liquid state at ordinary temperatures 27 to 46°C. (80 to 115°F.) and pressures of 125 to 175 lb. per sq. in. Simplified flow of the process is shown in Fig. 6, and considerable details have been published.[1,2,3] A liquid stream of recycled isobutane joins with a liquid olefin-containing feed stream and is mixed with liquid hydrogen fluoride in a suitable reactor

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[1] FREY, *Chem. Met. Eng.*, **50**, 126, (1943).

[2] GERHOLD, *et al.*, *Trans. Am. Inst. Chem. Eng.*, **39**, 793, (1943).

[3] "Hydrofluoric Acid Alkylation," Phillips Petroleum Company, 1945.

provided with means for removal of the heat of reaction. The effluent from the reactor is conducted to a settler where the hydrogen fluoride catalyst settles to the bottom and is pumped back to the reactor. Dissolved acid is removed from the hydrocarbon stream by an azeotropic fractionator, and traces of organically combined fluorine by a catalytic treatment, for example, with bauxite. The resulting hydrocarbon mixture is then fractionated as desired (see Fig. 6).

TABLE IV.—SOME HYDROCARBONS FORMED IN THERMAL ALKYLATION[1]

Feed to Alkylation	Major Hydrocarbons Produced
Ethylene and propane	Isopentane and *n*-pentane; about 2:1 ratio iso:normal
Ethylene and *n*-butane	3-Methylpentane
Ethylene and isobutane	2,2-Dimethylbutane (neohexane)
Propylene and propane	2,3-Dimethylbutane and 2-methylpentane
Ethylene and cyclohexane	Ethylcyclohexane

Note: Both lighter and heavier hydrocarbons than the main constituent are also produced by side reactions.

[1] Courtesy Phillips Petroleum Company.

TABLE V.—SOME HYDROCARBONS FORMED IN HF ALKYLATION[1]

A. *Alkylation of Isobutane with Propylene*

Hydrocarbons Produced	Approximate % Present in Total Alkylate
2,4-Dimethylpentane	10–15
2,3-Dimethylpentane	40–50
Other hydrocarbons:	
Pentanes	Few per cent each
Hexanes	
2, 2, 4-Trimethylpentane and other isooctanes	
Isononanes, isodecanes, and isoundecanes	

B. *Alkylation of Isobutane with Butylenes*

Hydrocarbons Produced	Approximate % Present in Total Alkylate
2,2,4-Trimethylpentane	35–40
2,3,4-Trimethylpentane 2,3,3-Trimethylpentane	20–30
Other hydrocarbons:	
Isopentane	Few per cent each
2,3-Dimethylbutane	
2,4-Dimethylpentane, 2,3-dimethylpentane	
Dimethylhexanes	
Isononanes (including 2,2,5-trimethylhexane)	
Isodecanes	
Isoundecanes	

[1] Courtesy Phillips Petroleum Company.

Propylene, butylenes, amylenes, and higher olefins are suitable for use in this process:

$$\text{iso } C_4H_{10} + C_4H_8 \xrightarrow{HF} C_8H_{18}$$

The effluent hydrocarbons from the reactor are virtually completely saturated. Isoparaffins (*e.g.*, isobutane and isopentane) react readily under the conditions used, but normal paraffins are virtually inert, although they can be alkylated under relatively severe conditions. Table V gives data on the hydrocarbons produced in alkylation of isobutane with propylene and butylenes, hydrogen fluoride being used as catalyst. In each case, the greater part of the alkylate is composed of two or three principal hydrocarbons with minor amounts of various other hydrocarbons of both lower and higher molecular weight formed by splitting and rearrangement reactions.

Table VI.—Some Hydrocarbons Formed in $AlCl_3$-complex Alkylation[1]

Alkylation of Isobutane with Ethylene-propylene Mixture

Hydrocarbons Produced	Approximate % in Total Alkylate
2,3-Dimethylbutane	55–70
Other hydrocarbons:	
Isopentane	Few per cent each
Methylpentanes	
2,4-Dimethylpentane and 2,3-dimethylpentane	
2,2,4-Trimethylpentane, 2,3,4- and 2,3,3-trimethylpentanes	
Isononanes	
Isodecanes	
Isoundecanes	

[1] Phillips Petroleum Company.

For typical operating conditions and yields, see Table VII. The yields and quantities vary with the composition of the alkylation feed as well as with the operating conditions. Quality of product for aviation- or motor-fuel use is also influenced by operation. Olefin concentration is maintained low and isoparaffin concentration high by recycling a large volume of isobutane to mix with the feed to the unit. The hydrogen fluoride catalyst used is virtually anhydrous, containing 0.2 to 2.0 per cent water. It becomes diluted with a highly olefinic "acid-soluble" oil during use and is purified by continuous distillation of a small portion of the circulating acid stream.

The development of technics of using this acid for a catalyst on a commercial scale in the oil industry opens possibilities for its use as a catalyst in other chemical reactions. Corrosion of the steel equipment employed has been slight,[1] and problems of mechanical operation[2] and safety[3] of operation have been solved.

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[1] Holmberg and Prange, *Ind. Eng. Chem.*, **37**, 1030 (1945).

[2] Findlay, *Nat. Petroleum News*, **37**, No. 18, R 325 (1945).

[3] Benson, *Petroleum Ref.*, **22**, 448–452 (1943).

Sulfuric Acid Alkylation.—This operates in a manner very similar to hydrogen fluoride alkylation with the exception that lower temperatures are necessary to suppress oxidation and other reactions.[1,2,3]. The reaction is normally carried out by refrigerating the feed to −1 to 10°C. (30 to 50°F.). The acid used as catalyst preferably contains 2 per cent or less water and becomes diluted with hydrocarbon material to about 90 per cent strength, at which point it is discarded. The spent sulfuric acid can be reclaimed in special plants or can be used in refinery treating of various products.

TABLE VII.—TYPICAL OPERATIONS OF PARAFFIN-OLEFIN ALKYLATION PROCESSES[1]

Operating conditions	Thermal alkylation	HF alkylation	$AlCl_3$-complex alkylation
Molar isobutane-olefin ratio (feed)	2.7:1	4 to 8:1	3.5 to 8:1
Contact time, min	4.5	10–20	20
Reaction temperature, °F	930	70–115	100–130
Reaction pressure, lb. per sq. in.	5,000	125–175	400
Catalyst:			
In reactor, vol. %	None	45–60	35–45
Acid strength, % HF	....	85–95	
$AlCl_3$ content, % by wt	....	....	55–62
Charge and Yields:			
Hydrocarbons reacted	Ethylene Isobutane	Butylenes Amylenes Isobutane	Ethylene Propylene Isobutane
Total alkylate yield, lb. per lb. olefin reacted	1.3–1.4	1.5–2.0	2.6–2.8
Isobutane consumed, lb. per lb. olefin reacted	0.8	1.0–1.1	1.7–1.9
Conversion of olefin, %	95	100	95–98

[1] Phillips Petroleum Company.

$AlCl_3$ Complex Alkylation.—Another catalyst for paraffin alkylation is a liquid complex made from aluminum chloride and hydrocarbon oils. This complex normally contains 55 to 62 per cent by weight aluminum chloride. One plant is in commercial operation using this process. Isobutane is alkylated with a mixture of ethylene and propylene, the ratio of the lighter to the heavier olefin being about 4:1. The olefins for alkylation are supplied from propane cracking as described under Thermal Alkylation, being available for alkylation as a solution in isobutane. Flow of the process is very similar to that for HF alkylation and is indicated in Fig. 7. Recycle isobutane, olefin-containing isobutane, and catalyst are mixed and contacted in a mechanically stirred reactor. The catalyst is settled, and the hydrocarbon mixture is fractionated to remove propane, recycle isobutane, pentane, and heavy hydrocarbons. The product "diisopropyl alkylate" is a very high-quality ingredient for aviation fuels.

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[1] BIRCH, DUNSTAN, *et al.*, *Oil Gas J.*, **37**, No. 6, 49 (1938).

[2] BIRCH and DUNSTAN, *Trans. Faraday Soc.*, **35**, 1013 (1939).

[3] Various Oil Companies, *Oil Gas J.*, **38**, No. 27, 104 (1939).

$$\text{iso } C_4H_{10} + C_2H_4 \rightarrow C_6H_{14}$$

Table VI gives data on the composition of "diisopropyl alkylate." As with the other alkylates, one compound makes up the major part of the product, other compounds being formed by side reactions. Typical operation and yields are indicated in Table VII. As in the other processes, variation of operating conditions and feed stocks cause considerable change in both yield and composition of the product.

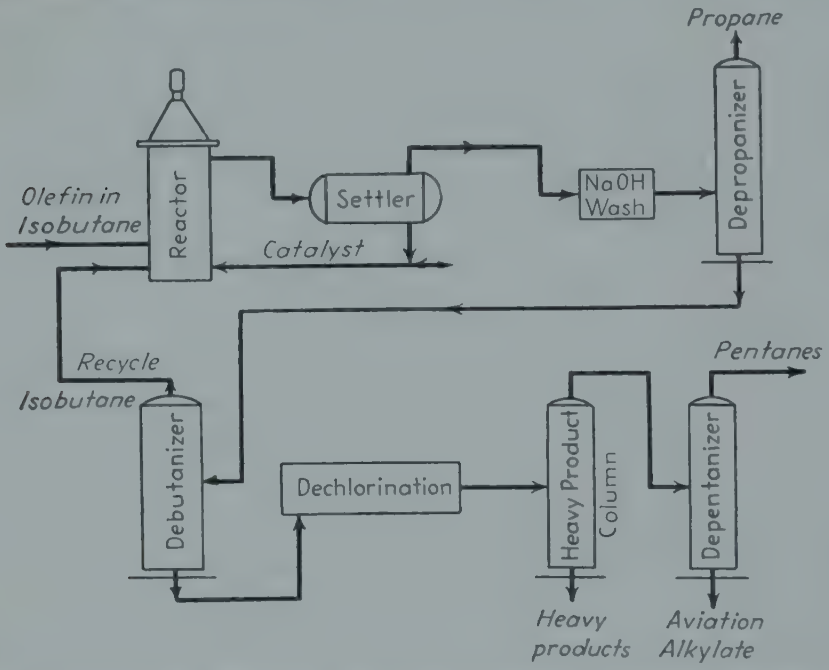

Propane
Olefin in Isobutane
Reactor
Settler
Catalyst
NaOH Wash
Depropanizer
Recycle Isobutane
Pentanes
Debutanizer
Dechlorination
Heavy Product Column
Depentanizer
Heavy products
Aviation Alkylate

FIG. 7.—Simplified flow diagram: $AlCl_3$ complex alkylation. (*Phillips Petroleum Company.*)

Olefin-aromatic Alkylation.—The manufacture of cumene (isopropylbenzene) as a blending agent for high-octane gasoline and of ethylbenzene as a raw material for styrene have been carried on during the Second World War on a very large scale. These catalytic alkylations may be formulated:

$$\underset{\text{Propylene}}{C_3H_6} + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{H_2SO} \underset{\text{Isopropylbenzene}}{C_3H_7 \cdot C_6H_5}$$

$$\underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{AlCl_3} \underset{\text{Ethylbenzene}}{C_2H_5 \cdot C_6H_5}$$

CUMENE

Preparation.—The formation of cumene or isopropylbenzene takes place at −1 to 10°C. (30 to 50°F.) and is accompanied[1] by polyalkylation giving some triisopropylbenzene which is fractionated out from the mono derivative and then converted to more isopropylbenzene by dealkylation-realkylation. Generally, aluminum chloride is employed for the reformer or dealkylation-realkylation catalyst and, of course, additional benzene.

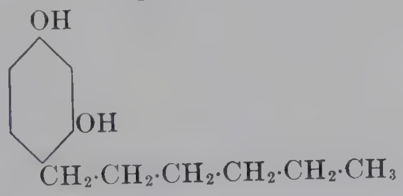
ETHYLBENZENE

Ethylbenzene has been made in a very large quantity in recent years as a step in the manufacture of styrene for GR-S synthetic rubber and for plastics. The reactions involved are essentially:

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5 \rightarrow C_6H_5C_2H_3 + H_2$$

Preparation.[2]—The gaseous ethylene is passed into the liquid benzene in presence of a metal chloride catalyst, such as aluminum chloride, at moderate temperatures (40 to 100°C.). However, other conditions such as vapor phase[3] and various catalysts[4] have been studied. As polyalkylation takes place, separation by distillation followed by dealkylation-realkylation of fresh benzene is practiced.

HEXYLRESORCINOL
CAPROKOL



The normal hexylresorcinol has been found to possess marked germicidal properties with a phenol coefficient of over 50. It is relatively nontoxic when administered by mouth and is partly excreted by the kidneys. A great number of acyl- and alkylresorcinols have been studied as regards their germicidal action.[5] The normal alkylresorcinols particularly have been found to be of value, a very pronounced increase being observed in the bactericidal power shown by these compounds up to normal nonylresorcinol. This action then decreases as the length of the chain increases becauses of the diminishing solubility of the alkylresorcinol. In Fig. 8 is shown the relationship between the atomic weight of the alkyl chain and the phenol coefficient (ratio of antibacterial

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[1] Egloff U. S. 2,010,948; 2,010,949 (1935); Ipatieff, U. S. 2,006,695 (1935); 2,039,798 (1936); "Catalytic Reactions at High Pressures and Temperatures," The MacMillan Company, New York, 1936. For fuller description and flow sheet, see 2d ed. (1938) of this volume, pp. 497–499, 527–530.

[2] Amos *et al.* (to Dow Chemical Company) U. S. 2,198,595 (1940); 2,222,012 (1940); 2,225,543 (1940); Kimberlin, U. S. 2,373,031 (1945); Francis and Reid, U. S. 2,364,203 (1944); Dow, *Ind. Eng. Chem.*, **34,** 1267–8 (1942); Anon, *Chem. Met. Eng.*, **51,** No. 2, 159–163 (1944), pictured flow sheet.

[3] Pardee and Dodge, *Ind. Eng. Chem.*, **35,** 273 (1943).

[4] Frey, U. S. 2,372,320 (1945); Schaad, U. S. 2,290,211 (1942).

[5] Dohme, Cox, and Miller, *J. Am. Chem. Soc.*, **48,** 1688 (1926); Schaffer and Tilley, *J. Bact.*, **14,** 259 (1927).

TABLE VIII.—COEFFICIENTS OF THE NORMAL RESORCINOLS WITH DIFFERENT STRAINS OF *Staphylococcus aureus*

Alkyl derivative	Phenol coefficients*		
	Strain No. 1	Strain No. 2	Strain No. 3
Ethyl	1.55	1.5	1.5
Propyl	3.9	3.7	3.7
Butyl	10.7	10	10.2
Amyl	30.2	30.2	30.6
Hexyl	97	98	98
Heptyl	295	280	280
Octyl	690	680	725
Nonyl	1,000	980	1,000

* At 25°C.

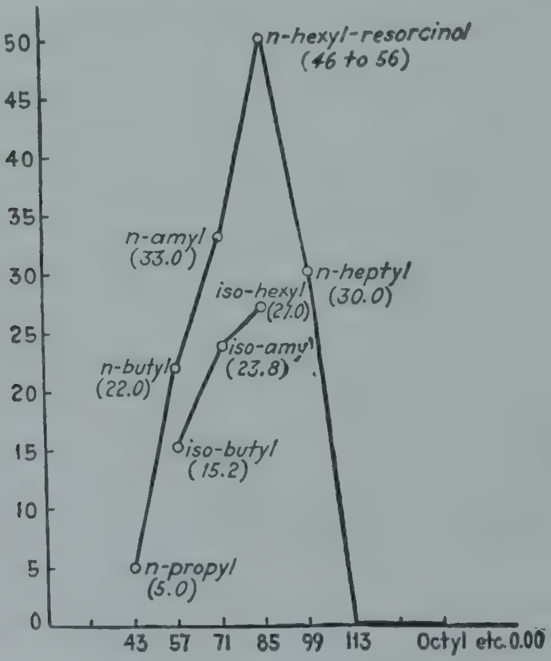
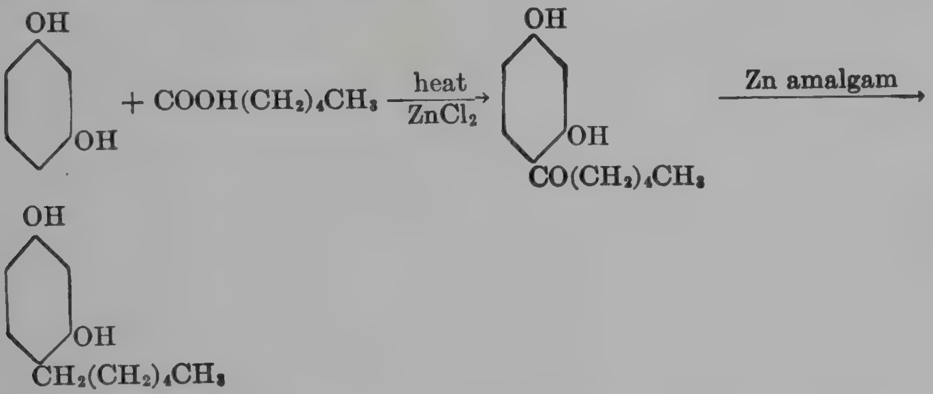


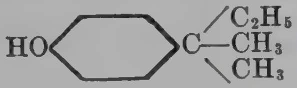
FIG. 8.—Bacterial activity of the alkylresorcinols. The curve is obtained by plotting the phenol coefficients (U. S. Hygienic Laboratory technic) as ordinates against the sum of the atomic weights of the atoms in the alkyl chain as abscissas. (*According to Dohme, Cox, and Miller.*)

power measured against *Eberthella typhosa* relative to that of phenol under the same conditions). Similar experiments with different strains of *Staphylococcus aureus* gave the results that are shown in Table VIII.[1]

Preparation.—According to various patents pertaining to the manufacture of hexylresorcinol, resorcinol and caproic acid are heated with a condensing agent, such as zinc chloride, whereby the intermediate ketone derivative is formed.[2] This is purified by vacuum distillation. By reduction with zinc amalgam and hydrochloric acid, impure hexylresorcinol results which can be purified by vacuum distillation.



TERTIARY AMYLPHENOL



Preparation[3]—The alkylation of phenols by alkyl halides is sometimes brought about through the intervention of a metal halide, *e.g.*, $AlCl_3$. When *tert*-amyl chloride is condensed with phenol and its homologues, no catalyst is necessary, although the presence of 3 to 5 per cent metal halide hastens the reaction. The following procedure may be employed for the preparation of *tert*-amylphenol in the absence of a catalyst.[4]

Eight moles of *tert*-amyl chloride are placed in a 5-liter flask with 8 moles of phenol and gently boiled under efficient reflux at a temperature of 80 to 100°C. for a period of 18 hr. During this period, a slow steady stream of hydrogen chloride gas is evolved. At the conclusion of 18 hr., the evolution of hydrogen chloride has ceased, and the contents of the flask are then vigorously refluxed for a period of ½ hr. at a temperature of 180°C. The material is then distilled at normal pressure through an efficient column. The distillation gives approximately the following cuts:

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[1] SCHAFFER and TILLEY, *ibid.*

[2] U. S. 1,649,670 (1927); Can. 264,841 (1926); Can. 264,842 (1926); Can. 265,025 (1926); Brit. 220,668 (1923).

[3] For some alkylated phenols, see WEINRICH, *Ind. Eng. Chem.*, **35**, 264 (1943); Turkington *et al.*, U. S. 2,353,282 (1944).

[4] U. S. 2,091,483 (1937).

Cut	B.p., °C.	Material	Weight, gm.	Softening point, °C.
1	60–100	*tert.*-Amylchloride	168	
2	100–200	Phenol	279	
3	200–248	Intermediate	30	About 45
4	248–255	*tert.*-Amylphenol	734	85
5	Residue	....	18	

Alkyl Bound to Metal.

LEAD TETRAETHYL
$Pb(C_2H_5)_4$

Lead tetraethyl is widely used for the prevention of knocking in high-compression gasoline engines—0.04 per cent tetraethyl lead being as efficient in this respect as 25 per cent of benzene. In order to prevent the deposition of lead in the exhaust sections of the engine, 3 parts by volume of tetraethyl lead is mixed with 2 parts of ethylene bromide ($CH_2Br.$-CH_2Br) or a mixture of ethylene bromide and ethylene chloride. The ethylene halide converts the lead oxide formed during the combustion into the volatile lead halide.

Preparation.—Lead tetraethyl is prepared industrially by the action of ethyl chloride on a lead sodium alloy.[1] Ethyl chloride reacts very rapidly with the alloy PbNa but not with the higher alloys. The final product of the reaction is very pure $Pb(C_2H_5)_4$. Very little is known regarding the mechanism of the reaction, and there are no indications of other alkylation products being formed as either intermediates or by-products. We may formulate the reaction as follows:

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

The process is simply the interaction of the alloy PbNa with ethyl chloride in an autoclave and in the absence of water or air. A little alcohol appears to catalyze the reaction.

The alloy must be uniformly subdivided,[2] preferably so as to pass a 10-mesh screen, and the temperature should not be higher than 70°C., except at the end, when 100°C. is permitted. The autoclave (Fig. 9) wherein the main reaction takes place must be equipped with a heating and cooling jacket and a strong stirring device so that the lead alloy can be brought into contact with the ethyl chloride and at a carefully controlled temperature. To start the reaction, it is necessary to warm up to about 35°C. with subsequent cooling to keep the temperature at 40 to 60°C. The time for completion of this reaction is from 2 to 6 hr. At the end, the excess ethyl chloride is distilled off and condensed. The lead tetraethyl is steam distilled from the reaction mass.

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[1] Kraus and Callis, U. S. 1,697,245; Fr. 796,791; Daudt, U. S. 2,091,114 (1937); Amick and Parmelee, U. S. 2,091,112 (1937); Ruddies, U. S. 2,277,781 (1942); Peck, U. S. 2,293,214 (1942); Sullivan, U. S. 2,148,138 (1939); Nourse, U. S. 2,310,806 (1943).

[2] Bake, U. S. 2,109,005 (1938).

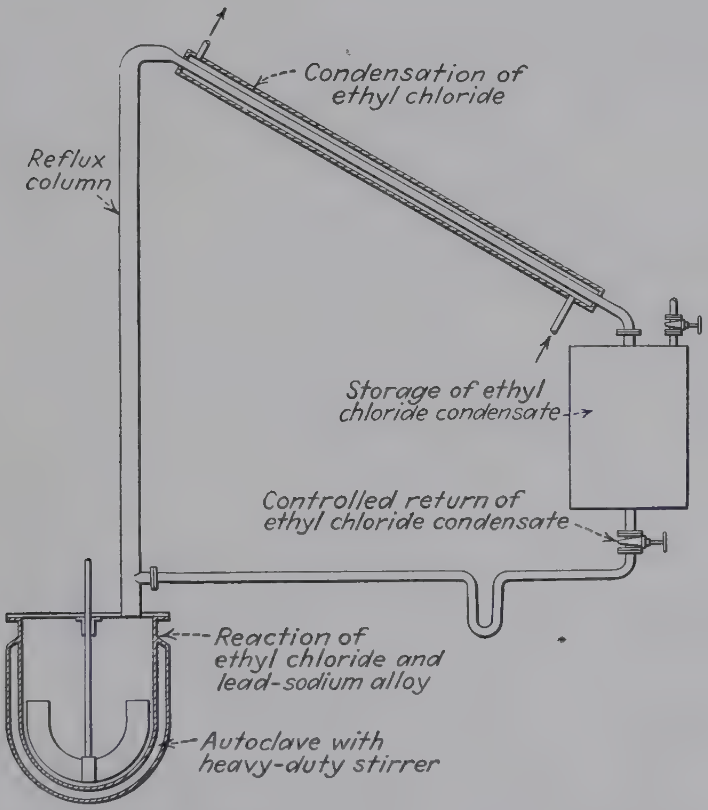

Condensation of ethyl chloride
Reflux column
Storage of ethyl chloride condensate
Controlled return of ethyl chloride condensate
Reaction of ethyl chloride and lead-sodium alloy
Autoclave with heavy-duty stirrer

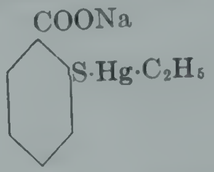
FIG. 9.—Flow diagram: preparation of lead tetraethyl.

Contrary to the action of the ethyl chloride, it is found that ethyl bromide and iodide do not react at all with PbNa but do react with $PbNa_2$ or, to less extent, with $PbNa_4$ if a small amount of water or alcohol is added from time to time. The yields are not so high as when the ethyl chloride is used. Depending upon the temperature, the product may contain a fair amount of $Pb_2(C_2H_5)_6$, which is not very stable and decomposes. These reactions may be written:

$$2PbNa_2 + 4C_2H_5Br \rightarrow Pb(C_2H_5)_4 + Pb + 4NaBr$$
$$3PbNa_2 + 6C_2H_5Br \rightarrow Pb_2(C_2H_5)_6 + Pb + 6NaBr$$
$$2Pb_2(C_2H_5)_6 \rightarrow 3Pb(C_2H_5)_4 + Pb$$

There is no evidence that $Pb(C_2H_5)_2$ is formed in these reactions, even as an intermediate.

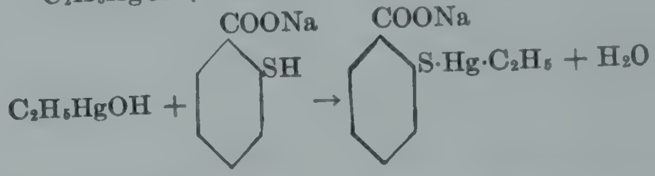
MERTHIOLATE
SODIUM ETHYLMERCURITHIOSALICYLATE



The antiseptic merthiolate, which contains 49 per cent of mercury in organic combination, is an example of an alkyl group bound to mercury. This product is much less toxic than mercuric chloride. It is an effective germicide for spore-bearing and nonspore-bearing bacteria, and it remains active in the presence of serum and tissue exudates. It is employed for sterilizing skin surfaces and mucous membranes and for disinfecting instruments.

This compound is prepared according to the patents by Kharasch,[1] and the following are the reactions involved:

$$C_2H_5MgBr + HgCl_2 \rightarrow C_2H_5HgCl + MgBrCl$$
$$C_2H_5HgCl + NaOH \rightarrow C_2H_5HgOH + NaCl$$



The proportions and the conditions used for making this compound are covered by Waldo's description, wherein ethylmercuric chloride, moistened with alcohol, is treated with 2 moles of caustic soda solution and with a 95 per cent alcoholic solution containing 1 mole of thiosalicylic acid.[2] After the solution is filtered, the ethylmercurithiosalicylic acid is precipitated by acidifying with 10 per cent sulfuric acid. Crystallization from 95 per cent alcohol results in a yield of 80 to 85 per cent. Exact neutralization of the pure acid with caustic soda gives merthiolate.

Kharasch, Marker, and Waldo studied the stability of ethylmercurithiosalicylic acid and related compounds and found that the higher homologues in the alkyl series are more stable than the lower members and that aryl groups are less stable than alkyl or aralkyl groups.[3,4] The germicidal value in relation to toxicity was decreased when the ethyl group was changed to methyl or isoamyl.

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[1] U. S. 1,589,599 (1926); Reissue 16,921 (1927); 1,672,615 (1928).

[2] Waldo, *J. Am. Chem. Soc.*, **53,** 992 (1931).

[3] Kharasch and Marker, *J. Am. Chem. Soc.*, **48,** 3130 (1926).

[4] Waldo, *loc. cit.*

CHAPTER X

ESTERIFICATION

By E. Emmet Reid

An ester is usually defined as a compound formed by substituting a group such as ethyl ($-C_2H_5$) for the ionizable H of an acid. In the older chemical literature, esters were commonly called "ethereal salts," and ethyl acetate was regarded as the analogue of sodium acetate. Doubt was thrown on this theory by a study of the esterification of mercaptan by acetic acid and of alcohol by thioacetic acid which react as follows:

$$CH_3CO{\cdot}OH + H{\cdot}SC_2H_5 \rightarrow CH_3COSC_2H_5 + H_2O$$
$$CH_3CO{\cdot}SH + H{\cdot}OC_2H_5 \rightarrow CH_3COOC_2H_5 + H_2S$$

According to this, the esterification reaction should be written the other way:[1]

$$CH_3CO{\cdot}OH + H{\cdot}OC_2H_5 \rightarrow CH_3COOC_2H_5 + H_2O$$

This view has been confirmed by a study of the esterification of methanol containing heavy oxygen, all of which went into the ester.[2] The ester should be regarded as having the acyl group substituted for the active hydrogen of the alcohol; ethyl acetate is acetyl-ethanol. However, the name ethyl acetate is too well established to be changed. Tertiary alcohols appear to divide between the alkyl and the hydroxyl: $R_3C{\cdot}OH$.[3] They differ greatly from primary and secondary alcohols in other respects.

In this chapter, esterification will be considered in the broadest sense as including all processes by which esters are produced. The importance of esters has increased enormously in recent years. The references cited are only a small fraction of those which might have been given; except in the historical part, they are limited to recent developments. Attention is called to articles by Keyes and Schotz on special phases of the subject and to two reviews.[4,5,6]

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[1] Reid, *Am. Chem. J.*, **43**, 489 (1910).

[2] Roberts and Urey, *J. Am. Chem. Soc.*, **60**, 2391 (1938); Mumm, *Ber.*, **72**, 1874 (1939).

[3] Cohen and Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941).

[4] Keyes, *Ind. Eng. Chem.*, **24**, 1096 (1932).

[5] Schotz, *Chem. Age*, **9**, 446 (1923).

[6] Reid, *Ind. Eng. Chem.*, **29**, 1344 (1937); Goldsmith, *Chem. Rev.*, **33**, 257–349 (1943).

It has been thought best to give the processes in broad outline, emphasizing the principles that underlie them. The principles are matters of general knowledge and do not change; the details of their application vary from time to time and from plant to plant and are usually kept secret as long as they are of private advantage. In fact, there is no absolutely best way to make any one ester such as ethyl acetate; an experienced and skillful operator can determine the most economical method for a certain scale of operation to produce a specified grade of ester with acetic acid, alcohol, and steam at certain prices, but, for another scale or with materials at other prices, an entirely different process may have the advantage. Anyone with a thorough understanding of the principles can apply them to special cases as they arise. Manufacturing processes are given for several esters, but these are presented as examples of how the principles may be applied, rather than as recipes.

To give an idea of the quantities of esters now being produced and consumed, a few figures are given for estimated current United States production, in millions of pounds per year:

Ethyl acetate	80	Alkyd resins	154
Butyl acetate	70	Cellulose acetate	204
Dibutyl phthalate	50	Cellulose xanthate	300

Cellulose nitrate, glyceryl trinitrate, vinyl acetate, and ethylidene diacetate are in the same class.

I. ESTERIFICATION REACTIONS

A number of reactions by which esters are produced is listed. These may be divided into groups—those in which two compounds react to give an ester and a second compound, as is the case when an acid reacts with an alcohol, and those in which an ester is formed by the addition of one compound to another, as when ethylene is taken up by sulfuric acid.

In direct esterification, an alcohol reacts with an acid, either organic or inorganic:

$$\underset{\text{Acetic Acid}}{CH_3COOH} + \underset{\text{Ethyl Alcohol}}{HOC_2H_5} \rightleftarrows \underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5} + H_2O \tag{1}$$

$$C_2H_5OH + HNO_3 \rightarrow \underset{\text{Ethyl Nitrate}}{C_2H_5ONO_2} + H_2O \tag{2}$$

$$C_2H_5OH + HO{\cdot}SO_2{\cdot}OH \rightleftarrows \underset{\text{Monoethyl Sulfate}}{C_2H_5O{\cdot}SO_2{\cdot}OH} + H_2O \tag{3}$$

Closely allied with direct esterification are alcoholysis, in which an alcohol displaces another alcohol, and acidolysis, in which an acid drives out another acid:

$$CH_3COOC_2H_5 + HOCH_3 \rightleftarrows CH_3COOCH_3 + HOC_2H_5 \tag{4}$$

$$CH_3COOC_2H_5 + C_5H_{11}COOH \rightleftarrows C_5H_{11}COOC_2H_5 + CH_3COOH \tag{5}$$

An exchange of alkyls may take place between two esters:

$$\underset{\text{Ethyl Benzoate}}{C_6H_5COOC_2H_5} + \underset{\text{Benzyl Acetate}}{CH_3COOCH_2C_6H_5} \rightleftarrows \underset{\text{Benzyl Benzoate}}{C_6H_5COOCH_2C_6H_5} + \underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5} \tag{6}$$

These reactions appear to be much like those which take place with inorganic acids, bases, and salts, but the resemblance is in form only, as the mechanisms are probably far different.

An amide, which is the nitrogen analogue of an acid, may react with an alcohol or with an amine:

$$CH_3CONH_2 + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + NH_3 \tag{7}$$

$$CH_3CONH_2 + RNH_2{\cdot}HCl \rightarrow CH_3CONHR + NH_4Cl \tag{7a}$$

An acid anhydride or chloride may react with an alcohol or phenol or their sodium derivatives:

$$C_2H_5OH + (CH_3CO)_2O \rightarrow CH_3COOC_2H_5 + CH_3COOH \tag{8}$$

$$(CH_3)_3COH + (CH_3CO)_2O \rightarrow CH_3COOC(CH_3)_3 + CH_3COOH \tag{9}$$

$$C_6H_5ONa + (CH_3CO)_2O \rightarrow CH_3COOC_6H_5 + CH_3COONa \tag{10}$$

$$C_2H_5OH + ClCOCl \rightarrow C_2H_5OCOCl + HCl \tag{11}$$

$$C_2H_5OH + C_2H_5OCOCl \rightarrow (C_2H_5O)_2CO + HCl \tag{12}$$

$$3C_2H_5ONa + Cl_3PO \rightarrow (C_2H_5O)_3PO + 3NaCl \tag{13}$$

$$C_6H_5ONa + CH_3COCl \rightarrow C_6H_5OCOCH_3 + NaCl \tag{14}$$

The salt of an acid may react with an alkyl or aralkyl halide:

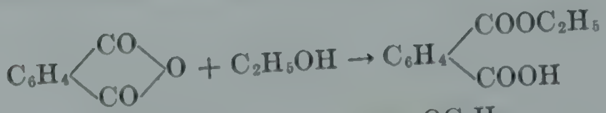
$$\underset{\text{Sodium Acetate}}{CH_3COONa} + C_2H_5Br \rightarrow \underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5} + NaBr \tag{15}$$

$$CH_3COONa + \underset{\text{Benzyl Chloride}}{C_6H_5CH_2Cl} \rightarrow \underset{\text{Benzyl Acetate}}{CH_3COOCH_2C_6H_5} + NaCl \tag{16}$$

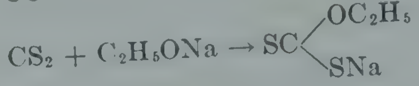
In all the above, the formation of the by-product water, hydrogen chloride, or sodium chloride is very important from the energy standpoint. Thermodynamically, reactions (13), (14), and (16), for example, may be regarded as syntheses of sodium chloride, since the intense affinity of sodium and chlorine for each other is the driving force that causes these reactions to go. The yield of sodium chloride is quantitative; the other parts of the original molecules may get together to form the ester, or they may not.

In the second group are placed reactions in which esters are formed by the addition of two compounds. In these reactions, the driving force may be some sort of strained condition in a double bond or the possibility of rearranging the atoms so as better to satisfy their affinities.

As a sort of transition between the two groups, we may put the reaction of the anhydride of a dibasic acid with an alcohol or a sodium alcoholate:



(17)



$$CS_2 + C_2H_5ONa \rightarrow SC\begin{matrix}OC_2H_5\\SNa\end{matrix}$$

(18)

In reaction (17), an ester and an acid are formed as in (9), but, being parts of the same molecule, they remain together.

In esterification according to reaction (1), a molecule of water is eliminated, part coming from the alcohol and part from the acid. If a whole molecule of water is eliminated from either the alcohol or the acid previously, an ester can be formed by simple addition. Thus, ketene ($CH_2{:}CO$) is acetic acid minus a molecule of water, and phenyl isocyanate bears the same relation to phenylcarbamic acid:

$$CH_3COOH - H_2O = CH_2{:}CO \qquad (19)$$

$$C_6H_5NH{\cdot}CO{\cdot}OH - H_2O = C_6H_5N{:}C{:}O \qquad (20)$$

Ketene and phenyl isocyanate both add to an alcohol to form an ester:

$$CH_2{:}CO + C_2H_5OH = CH_3COOC_2H_5 \qquad (21)$$

$$C_6H_5N{:}CO + C_2H_5OH \rightarrow C_6H_5NHCOOC_2H_5 \qquad (22)$$

Diketene gives the acetoacetate

$$(CH_2CO)_2 + C_2H_5OH \rightarrow CH_3COCH_2COOC_2H_5 \qquad (22a)$$

These reactions take place spontaneously, the driving force being the unsaturation.

Ethylene is alcohol minus a molecule of water and adds directly to acids:

$$CH_2{:}CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H \qquad (23$$

$$CH_2{:}CH_2 + CH_3COOH \rightarrow CH_3COOC_2H_5 \qquad (24$$

The addition of an acid such as acetic takes place only in the presence o sulfuric acid or other catalyst, and it is probably more correct to sa that the ethyl acetate is formed by the action of the acetic acid on th ethylsulfuric acid in the equation above.

Subtracting a molecule of water from the unstable ethylidene glycol we have the hypothetical vinyl alcohol; another is taken away an acetylene is left:

$$CH_3{\cdot}CH(OH)_2 - H_2O = CH_2{:}CHOH \qquad (25$$

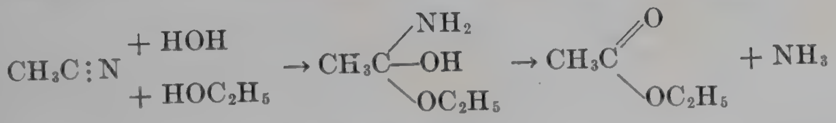
$$CH_2{:}CHOH - H_2O = CH{\vdots}CH \qquad (2$$

Acetylene takes up 1 molecule of acetic acid to give vinyl acetate c 2 to form ethylidene acetate:

$$CH{\vdots}CH + CH_3COOH \rightarrow CH_3COOCH{:}CH_2 \qquad (2$$

$$CH{\vdots}CH + 2HOCOCH_3 \rightarrow CH_3CH(OCOCH_3)_2 \qquad (2$$

The passage of a nitrile into an ester involves the addition of 1 molecule of water and 1 of alcohol and the loss of 1 of ammonia:

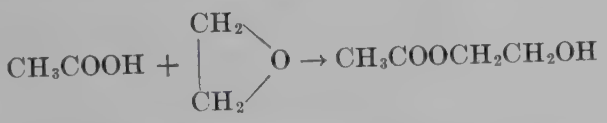


(29)

To avoid assuming a third-order reaction, we may assume that the molecule of water is taken up to form the amide, which is then esterified [reaction (7)], or that the alcohol is added to give an iminoester, which is hydrolyzed:

$$CH_3C\vdots N + H_2O \rightarrow CH_3CONH_2$$
$$CH_3CONH_2 + HOC_2H_5 \rightarrow CH_3COOC_2H_5 + NH_3$$
$$CH_3C\vdots N + HOC_2H_5 \rightarrow CH_3C(:NH)OC_2H_5$$
$$CH_3C(:NH)OC_2H_5 + H_2O \rightarrow CH_3COOC_2H_5 + NH_3$$

Subtracting a molecule of water from ethylene glycol, we have ethylene oxide, which adds to an acid to give a mono-ester of glycol:



(30)

There is another reaction that does not come under any one of these classes, and that is the combination of 2 molecules of an aldehyde to give 1 of an ester:

$$2CH_3CHO \rightarrow CH_3COOCH_2CH_3 \qquad (31)$$

Carbon monoxide, the anhydride of formic acid, may combine with an alcohol to give a formic ester:

$$CO + ROH \rightarrow HCOOR \qquad (32)$$

Carbon monoxide may unite with an alcohol to give an acid, which may then react with another molecule of the alcohol to form an ester:

$$CO + CH_3OH \rightarrow CH_3COOH \qquad (33)$$
$$CO + 2CH_3OH \rightarrow CH_3COOCH_3 + H_2O \qquad (34)$$

Esterification with Inorganic Acids.—In esterification by inorganic acids, theory has received little attention, but practice has gone far, particularly in nitration [reaction (2)]:

$$C_2H_5OH + HNO_3 \rightarrow C_2H_5ONO_2 + H_2O$$
$$\underset{\text{Glycol}}{C_2H_4(OH)_2} + 2HNO_3 \rightarrow \underset{\text{Glycol Dinitrate}}{C_2H_4(ONO_2)_2} + 2H_2O$$
$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3HNO_3 \rightarrow \underset{\text{Glyceryl Trinitrate}}{C_3H_5(ONO_2)_3} + 3H_2O$$
$$\underset{\text{Cellulose Unit}}{[C_6H_7O_2(OH)_3]} + 3HNO_3 - \underset{\text{Nitrocellulose Unit}}{[C_6H_7O_2(ONO_2)_3]} + 3H_2O$$

There are two cases: the alcoholic compound, such as glycerol, may dissolve in the acid or may be insoluble, as is the case with cellulose.

In both cases, the operations are simple, though the working out of the exact details for obtaining the desired products in high purity and good yields has required much painstaking experimentation. So-called *mixed acid*, which is employed in nitrations, is a mixture of nitric and sulfuric acids and may contain water or sulfur trioxide, the concentrations of these being accurately adjusted to give the desired intensity of reaction.

In the nitration of cellulose, the reaction is carried out under accurately controlled conditions, so that a product is obtained with the desired properties. These properties are different according to the use for which the material is destined. The product, nitrocotton, is always classified by the percentage of nitrogen that it contains. In carrying out the reaction, the most important thing is uniformity of action, since the value of the product is largely dependent on its approach to homogeneity.

A monosulfate is formed when sulfuric or chlorsulfonic acid reacts with an alcohol [reaction (3)]:

$$C_2H_5OH + HO{\cdot}SO_2{\cdot}OH \leftrightharpoons C_2H_5O{\cdot}SO_2OH + H_2O \qquad (3)$$
$$C_2H_5OH + Cl{\cdot}SO_2{\cdot}OH \rightarrow C_2H_5O{\cdot}SO_2OH + HCl$$

This reaction is used for converting the higher alcohols into their monosulfates, which have recently come into use as detergents and wetting agents.

$$C_{12}H_{25}OH + H_2SO_4 \rightarrow C_{12}H_{25}OSO_2OH + H_2O$$

The reactions of alcohols with nitric and sulfuric acids slow down and come to a standstill when the water formed accumulates. They are aided by an excess of sulfuric acid or sulfur trioxide.

An alkyl monosulfate may be made in quite a different manner by the addition of an unsaturated hydrocarbon to sulfuric acid, as represented in reaction (23):

$$CH_2{:}CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_2OH \qquad (23)$$

The addition takes place on simple contact of the hydrocarbon with the acid, but the speed of the reaction depends on the strength of the acid and the nature of the hydrocarbon. To keep down polymerization and isomerization of the hydrocarbons, the temperature is kept relatively low, usually below about 40°C. and commonly lower than that—even down to 0°C. The sulfuric acid may be from 10 to 100 per cent or may even contain some sulfur trioxide, the strength used depending on the hydrocarbon. Some of the terpenes react with the 10 per cent acid, while ethylene reacts extremely slowly with acid of less than 90 per cent. When a reactive hydrocarbon is shaken with the 10 per cent acid, the alkylsulfuric acid may be formed and hydrolyzed immediately, so that apparently the hydrocarbon simply takes up a molecule of water. If the right strength of sulfuric acid is chosen, the absorption may be made selective, so that certain unsaturated hydrocarbons are taken out of a mixture. Thus, if a mixture of ethylene and propylene is brought into contact with 85 per cent sulfuric acid, the propylene is completely absorbed and the ethylene practically untouched. The normal butylenes are absorbed by somewhat weaker sulfuric acid than is propylene, but the difference in reactivity is not sufficient for a sharp separation.[1] Isobutylene reacts particularly readily and may be selectively absorbed by 65 per cent sulfuric acid with cooling.

The best known case of the use of this reaction is the manufacture of "Petrohol," or isopropyl alcohol, from cracking still gases. The more easily condensable constituents of the still gas, the butylenes and higher, are removed by condensation or absorption; the residue, consisting of ethylene and propylene (with some hydrogen, methane, and ethane), is cooled and passed up through towers over the packing of which 85 per cent sulfuric acid flows. The acid, which is largely isopropylsulfuric acid, is drawn off at the bottom of the tower, diluted with water, and boiled. The isopropylsulfuric acid is hydrolyzed, and the isopropyl alcohol distills over. Under 100 lb. pressure a second molecule of propylene is taken up to form isopropyl sulfate, which separates on the addition of water.[2]

Current production by this method is about 85,000,000 gal. isopropanol and 70,000,000 gal. ethanol per year.

Ethyl sulfate may be obtained by distilling the ethylsulfuric acid at 10 mm.[3] Methyl sulfate may be made by combining sulfur trioxide directly with methyl ether.[4]

With the addition of an organic acid, or a salt from which one may be set free, to the alkylsulfuric acid, an ester of the organic acid is obtained.[5]

Esterification with Organic Acids.—This is esterification in its narrow sense and is what comes to mind when the term is used. It has long excited the curiosity of chemists and has been extensively studied by both organic and physical chemists. It has been one of the most useful reactions in preparative organic chemistry, one of the best examples of the application of the mass-action law, and one of the most baffling problems in homogeneous catalysis.

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[1] Apgar, U. S. 1,846,666; N.-V. de Bataafsche Petroleum-Maatschappij, Ger. 541,628; Fr. 718,943; 730,829; Dutch 25,123; 27,237; Brooks, U. S. 1,879,599; 1,894,661; 1,904,200; Davis, U. S. 1,844,208; Engs and Moravec, U. S. 1,854,581; Can. 323,969; Markovich and Pigulerskii, *J. Russ. Phys. Chem. Soc.*, **24,** 880 (1892); **25,** 599 (1893); Taveau, U. S. 1,845,007.

[2] Brooks, U. S. 1,919,617.

[3] Kuh, U. S. 1,411,215; Lillienfeld, U. S. 1,074,633; Ger. 272,339.

[4] Haworth and Irvine, U. S. 1,401,693.

[5] Archibald and Lebo, U. S. 1,844,536; Ellis and Cohen, U. S. 1,365,049; 1,365,050; Frolich and Young, U. S. 1,877,291; Hunt, Brit. 173,538; 173,786; Lommel and Engelhardt, U. S. 1,903,868; Merley and Spring, U. S. 1,924,615; Shukoff, Brit. 20,526; Simon, *Compt. rend.*, **176,** 583 (1923); Spring, U. S. 1,924,575; Wilson, U. S. 1,979,575.

That an alcohol heated with an acid gives an ester and that the ester heated with water reverts to the alcohol and acid has long been a well-known fact; *i.e.*, the reaction

$$C_2H_5OH + HOCOCH_3 \rightleftarrows C_2H_5OCOCH_3 + H_2O$$

is reversible, but it remained for Berthelot and Péan de St. Gilles, in 1862, to make exact measurements on it and determine the equilibrium point.[1] The numerous experiments that they performed were simple but were carried out with painstaking accuracy. They heated ethyl alcohol with one equivalent of acetic acid at 100, 170, and 200°C. for definite intervals of time, which were increased until the ester content of the mixture became constant. The reactants were weighed into small glass tubes, which were sealed off, heated the requisite time, cooled, broken open, and the remaining acid titrated. At 100°C. in 200 hr., 65.6 per cent of ester was formed; at 170° in 24 hr., 66.5 per cent; and at 200° in the same time, 67.3 per cent. Starting from the other end, they heated ethyl acetate with an equivalent of water and found that equilibrium was reached at the same point. They tried several equivalents of acid to one of the alcohol and found that higher percentages of it esterified. Similarly, they showed that two or more equivalents of alcohol to one of acid gave correspondingly higher amounts of ester. They performed similar experiments with other alcohols and acids and obtained similar results. They left some samples of the alcohol-acetic acid mixture sealed up at room temperature for 15 years and found 65.2 per cent of ester. Their results were discussed by Van't Hoff, Thomsen, and others and found to be in accordance with mass-action law.[2]

Writing the reaction after the manner of physical chemists as an equilibrium, we have

$$\frac{[\text{Ester}] \times [\text{water}]}{[\text{Acid}] \times [\text{alcohol}]} = K$$

This means that the product of the concentrations of ester and water divided by the product of the concentrations of acid and alcohol is equal to a constant. The constancy of this K has been questioned.[3] Its value

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[1] BERTHELOT, *Ann. chim.* [3], **66,** 110 (1862); **68,** 274 (1863); [5], **14,** 437 (1878); **15,** 220, 238 (1878); *Bull. soc. chim.* [2], **31,** 341 (1879); BERTHELOT and PÉAN DE ST. GILLES, *Ann. chim.* [3], **65,** 385 (1862); **66,** 5 (1862); **68,** 225 (1863).

[2] VAN'T HOFF, *Ber.*, **10,** 669 (1877); THOMSEN, *Ber.*, **10,** 1023 (1877); URECH, *Ber.*, **19,** 1700 (1886).

[3] CORSO and DURRUTY, *Anales asoc. quim. Argentina*, **20,** 140 (1932); KNOBLAUCH, *Z. physik. Chem.*, **22,** 268 (1897); POZNANSKI, *Roczniki Chem.*, **8,** 377 (393 Eng.) (1928); SWIETOSLAWSKI, *J. Phys. Chem.*, **37,** 701 (1933); CORIA, *Rev. facultad cienc. quim.* (*Univ. La Plata*), **10,** 67 (1935).

TABLE I.—RATES AND LIMITS OF ESTERIFICATION
Acetic Acid at 155°C. with Various Alcohols

No.	Alcohol	Per cent conversion		K
		1 hr.	Limit	
1	Methyl	55.59	69.59	5.24
2	Ethyl	46.95	66.57	3.96
3	Propyl	46.92	66.85	4.07
4	Butyl	46.85	67.30	4.24
5	Allyl	35.72	59.41	2.18
6	Benzyl	38.64	60.75	2.39
7	Dimethylcarbinol	26.53	60.52	2.35
8	Methylethylcarbinol	22.59	59.28	2.12
9	Diethylcarbinol	16.93	58.66	2.01
10	Methylhexylcarbinol	21.19	62.03	2.67
11	Diallylcarbinol	10.31	50.12	1.01
12	Menthol	15.29	61.49	2.55
13	Trimethylcarbinol	1.43	6.59	0.0049
14	Dimethylpropylcarbinol	2.15	0.83	0.000070
15	Phenol	1.45	8.64	0.0089
16	Thymol	0.55	9.46	0.0192

is altered by the presence of salts.[1] For the acetic acid-water mixture, this would be

$$\frac{66.5 \times 66.5}{33.5 \times 33.5} = K = 3.94$$

Menschutkin made a comparative study of a large number of acids and alcohols.[2] He found striking differences among primary, secondary, and tertiary alcohols, as to both the rates and the limits of esterification. Table I gives some of his results for acetic acid heated to 155°C. with equivalent amounts of various alcohols. The mixtures were heated for 1 hr. to find the relative rates and for a much longer time—usually 100 or 200 hr.—to get the limits.

It will be observed that, of all the alcohols studied, methyl shows the greatest initial velocity and the highest limit. The primary alcohols, ethyl, propyl, and butyl, have approximately the same initial velocities and limits but are inferior to methyl alcohol in both of these respects. Allyl alcohol is much slower than propyl, the saturated alcohol with the same number of carbon atoms. The presence of the phenyl group in benzyl has a retarding influence.

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[1] CANTELO and BILLINGER, *J. Am. Chem. Soc.*, **50**, 3212 (1928); SCHLESINGER, *Ber.*, **59**, 1965 (1926); SCHLESINGER and MALKINA-OKUN, *Ber.*, **60**, 1479 (1927).

[2] MENSCHUTKIN, *Ann.*, **195**, 334 (1879); **197**, 193 (1879); *Ber.*, **13**, 162 (1880); *Ann. chim.* (5), **23**, 14 (1881); **30**, 81 (1883); *Z. physik. Chem.*, **1**, 611 (1887); **9**, 237 (1892); *Ber.*, **42**, 4020 (1909).

The secondary alcohols (Nos. 7 to 12, Table I) are markedly lower than the primary in both initial velocity and limit but vary considerably among themselves. The tertiary alcohols (Nos. 13 to 14) show little esterification in 1 hr. and hardly any more in 100. In the case of the tertiary alcohols, the "limit" is seldom if ever reliable, since there is such a great tendency for these alcohols to split off water, leaving unsaturated hydrocarbons. It is not unusual with tertiary alcohols to find less ester after long than after short heating. Phenol and thymol, which may be regarded as tertiary alcohols but which cannot split off water, show low initial velocities but comparatively high limits.

As was pointed out by Michael, the three classes of alcohols are not always sharply separated as in the above examples; *i.e.*, some tertiary alcohols may go as fast and as far as certain secondaries, and primary alcohols have been found that do not esterify so readily or so completely as some secondary.[1] The general statement is that the more branched the carbon chain and the nearer the branches are to the hydroxyl group the slower will be its esterification and the lower the limit. Many other more or less similar studies have been made.[2]

Similar experiments were made by Menschutkin, using isobutyl alcohol with a variety of acids. Some of the results are given in Table II.

By examining the data for the per cent conversion for the first hour, we are struck with the similarity of their relationships to those observed in Table I. Formic acid reacts much more rapidly than the other straight-chain acids, and the branched-chain acids trimethylacetic and dimethylethylacetic are particularly slow. The introduction of a phenyl group, as in Nos. 9 and 10, does not retard esterification, but the purely aromatic acids benzoic and *p*-toluic are very slow. Contrasting cinnamic with phenylpropionic, we see that the double bond has a marked retarding effect. Maleic acid is esterified fourteen times as rapidly as fumaric.[3] An alcohol dissolved in excess of formic acid is esterified several thousand times as rapidly as in acetic.[4]

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[1] Michael, *Ber.*, **42,** 310 (1909); **43,** 464 (1910); Michael and Oechslin, *Ber.*, **42,** 317 (1909); Michael and Wolgast, *Ber.*, **42,** 3157 (1909).

[2] Cauquil, *J. chim. phys.*, **23,** 586 (1926); Charabot and Hébert, *Bull. soc. chim.* [3], **25,** 884, 955 (1901); Dobrochotow, *J. Russ. Phys. Chem. Soc.* [6], **27,** 341 (1895); *Z. physik. Chem.*, **23,** 555 (1897); Doleman, Thesis, Mass. Inst. Tech., 1931; Marckwald and McKenzie, *Ber.*, **32,** 2130 (1899); Meisenheimer and Schmidt, *Ann.*, **475,** 157 (1929); Panoff, *J. Russ. Phys. Chem. Soc.*, **35,** 93 (1903); Petrenko-Kritschenko, Bogatsky, and Lubman, *Z. physik. Chem.*, **115,** 289 (1925); Prager, *Z. physik. Chem.*, **66,** 292 (1909); Reicher, *Ann.*, **228,** 257 (1885); Skrabal and Matievic, *Monatsh.*, **45,** 39 (1924); Vavon and Guedon, *Bull. soc. chim.* [4], **47,** 901 (1930); Wilcox and Brunel, *J. Am. Chem. Soc.*, **38,** 1821 (1916).

[3] Schwab, *Rec. trav. chim.*, **2,** 46 (1883).

[4] Kailan and coworkers, *Monatsch.*, **62,** 284 (1933); **63,** 155 (1933); **68,** 109 (1936).

Although, with the alcohols, slow esterification and a low limit go together, it is quite otherwise with the acids. Thus, dimethylethylacetic acid gives only 3.4 per cent of ester in 1 hr. but finally, after 500 or 600 hr., reaches a limit that is even higher than the limit for acetic acid. The unsaturated acids, cinnamic and sorbic, start off much more slowly than the corresponding saturated acids but go somewhat further. Formic acid, which has an extremely high initial rate, has a relatively low limit.

TABLE II.—RATES AND LIMITS OF ESTERIFICATION, ISOBUTYL ALCOHOL WITH VARIOUS ACIDS AT 155°C.

No.	Acid	1 hr.	Limit	K
1	Formic	61.69	64.23	3.22
2	Acetic	44.36	67.38	4.27
3	Propionic	41.18	68.70	4.82
4	Butyric	33.25	69.52	5.20
5	Isobutyric	29.03	69.51	5.20
6	Methylethylacetic	21.50	73.73	7.88
7	Trimethylacetic	8.28	72.65	7.06
8	Dimethylethylacetic	3.45	74.15	8.23
9	Phenylacetic	48.82	73.87	7.99
10	Phenylpropionic	40.26	72.02	7.60
11	Cinnamic	11.55	74.61	8.63
12	Benzoic	8.62	72.57	7.00
13	*p*-Toluic	6.64	76.52	10.62

A special case which has received much attention is that of 2,6-disubstituted benzoic acids (*hindered acid*), which, as shown by Victor Meyer and others, are esterified with extreme slowness.[1] Even one ortho group has a marked effect; methyl reduces the esterification velocity of benzoic acid by 68 per cent, ethyl by 80 and propyl by 83.[2]

The experiments cited above were with equivalent amounts of alcohols and acids, but, by assuming that the mass-action law holds, we can calculate the percentage of an alcohol that will be esterified when more than one equivalent of acid is used. If x is the percentage of ester formed, it will also be the percentage of water, and we have, when n equivalents of alcohols are used to 1 of acid:

$$\frac{[\text{Ester}] \times [\text{water}]}{[\text{Acid}] \times [\text{alcohol}]} = K = \frac{x^2}{(100 - x)(100n - x)}$$

In the case of acetic acid and ethyl alcohol, K was found to be 3.94.

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[1] MEYER, *Ber.*, **27**, 510 (1894); **28**, 182, 2773 and 3197 (1895); HUFFERD and NOYES, *J. Am. Chem. Soc.*, **43**, 925 (1921); PRAGER, *J. Am. Chem. Soc.*, **30**, 1908 (1908); ROSANOFF and PRAGER, *J. Am. Chem. Soc.*, **30**, 1895 (1908).

[2] ZWECKER, *Ber.*, **68**, 1289 (1935).

If we take $K = 3.94$ and use 5 moles of alcohol to 1 of acetic acid, this becomes

$$x^2 = 3.94\ (100 - x)(500 - x)$$

Solving this, we get 94.5 per cent. In an actual experiment, Berthelot and Péan de St. Gilles heated 1 mole of acetic acid with 5 of ethyl alcohol for 83 hr. at 100°C. and found 96.6 per cent of it esterified. In another experiment in which the proportions were reversed, they found 97.2 per cent of the alcohol esterified in 330 days at room temperature. Considering the difficulty of handling volatile liquids without loss and the limited accuracy of titration methods, these results are in close agreement with the calculated. It is evident, however, that no matter what excess of one reactant, the other is never completely used up.

II. SPEEDING UP ESTERIFICATION

If from a mixture of acetic acid and ethyl alcohol, standing at room temperature, samples are taken out and titrated every now and then, a slow decrease in acidity can be observed, but days and even months will elapse before the minimum value, or limit, is reached. Like most other reactions, the speed of esterification approximately doubles with a 10°C. rise in temperature. According to this rule, it should go sixty-four times as rapidly at the boiling point of alcohol as at 18°C., going as far in a single minute at the higher temperature as in an hour at the lower. Hence, it has been customary to use heat to speed up esterification reactions. From the figures given above, it appears that the limit is not reached in an hour even at 155°C., a temperature inconveniently high when low-boiling acids and alcohols are concerned. Except in the case of a high-boiling alcohol such as glycerol with a high-boiling acid such as stearic, esterification cannot be effected at atmospheric pressure in a reasonable time without some other means of speeding up the reaction. Fortunately, there is such a means.

Catalytic Esterification.—It has long been known that the process of esterification may be enormously hastened by the addition of a strong acid, such as sulfuric or hydrochloric. The limit of the reaction is not greatly altered.[1] To two samples of the acetic acid-alcohol mixture, 0.67 and 4.5 per cent of hydrogen chloride were added. After 10 hr. at 100°C., the limits were found to be 67.6 and 68.8 per cent, respectively.

Ostwald found a close relation between the activity of an acid in the hydrolysis of methyl acetate and in the inversion of sugar with its conductivity and concluded that the acceleration is due to the hydrogen ion.[2] Some of his figures are given in Table III.

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[1] BERTHELOT and PÉAN DE ST. GILLES, *Ann. chim. phys.* [3], **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

[2] OSTWALD, *J. prakt. Chem.* [2], **28**, 449 (1883); **30**, 93 (1884); **35**, 122 (1887).

The same figures may be taken as representing the relative efficiency of these acids as catalysts in the reverse reaction of esterification. It will be noted that the very strong acids have nearly the same effect whereas the organic acids with the exception of oxalic are poor catalysts. The introduction of chlorine into acetic acid greatly increases its strength. Sulfuric acid appears to be only slightly more than half as effective as hydrochloric, *i.e.*, if it is counted as dibasic, while ethylsulfuric and ethanesulfonic rank with the strongest.

Table III.—Relative Rates of Hydrolysis of Methyl Acetate with Various Acids as Catalysts

Acid	Rate of hydrolysis, %	Acid	Rate of hydrolysis, %
Hydrochloric	100	Malonic	2.87
Hydrobromic	89.3	Succinic	0.496
Nitric	91.5	Tartaric	2.30
Sulfuric	54.7	Formic	1.31
Ethylsulfuric	98.7	Acetic	0.345
Ethanesulfonic	97.9	Chloroacetic	4.3
Benzenesulfonic	99.0	Dichloroacetic	23.0
Oxalic	17.46	Trichloroacetic	68.2

In general practice, hydrochloric and sulfuric acids are the ones most commonly used, the former being in favor in the laboratory on account of its efficiency and the latter in the plant on account of its cheapness and because it is less corrosive on metals.[1] Sulfuric acid may cause the dehydration of an alcohol if used in too great an amount or at too high a temperature. Thus, cyclohexanol boiled 30 min. with 2 moles of acetic acid and 3 per cent by volume of sulfuric acid gave 30 per cent cyclohexene. The use of any strong acid as a catalyst may cause isomerization or destruction of a tertiary alcohol such as linalool.

Perchloric and phosphoric acids have been recommended.[2] Phosphoric acid is less efficient but also less destructive. The sulfonic acids, particularly those containing a considerable number of carbon atoms, are desirable catalysts on account of their high efficiency, solubility in the higher alcohols and acids, and less destructive action.[3] The most com-

[1] Mailhe, *Chem. Ztg.*, **37,** 777 (1913); Senderens and Aboulenc, *Compt. rend.*, **152,** 1671, 1855 (1911); **153,** 881 (1911); **155,** 168, 1254 (1912); **158,** 581 (1914); *Ann. chim.*, **18,** 145 (1922).

[2] Smith and Orton, *J. Chem. Soc.*, **95,** 1060 (1906); Trimble and Richardson, *J. Am. Chem. Soc.*, **62,** 1018 (1940); Holzverkohlungs-Industrie, Fr. 657,812; Brit. 320,113.

[3] Twitchell, Brit. 371,689; Ciocca and Semproni, *Ann. chim. applicata*, **25,** 319 (1935); Zaganiaris and Varvoglis, *Ber.*, **69,** 2277 (1936).

monly used is *p*-toluenesulfonic acid. Twitchell's reagent is a good catalyst; a wetting agent such as dodecanesulfonic acid is recommended.[1] Boron and silicon fluorides are excellent catalysts.[2] Dihydroxyfluoboric acid is efficient.[3] Acid chlorides are said to be better than hydrochloric acid.[4]

Acid salts, such as potassium bisulfate, and salts of strong acids with weak bases have been tried as catalysts,[5] but such activity as they have may be attributed to the hydrogen ions present in their solutions. Zinc chloride seems to enhance the effect of acids. The addition of a large amount of calcium chloride aids in the separation of water as a layer. Aluminum, ferric,[6] and magnesium chlorides[7] have been recommended.

Various patents claim the use of aluminum, cobalt, lead, magnesium tin, and zinc soaps.[8] Metals in the finely divided state, tin, manganese, bismuth, lead, silver, and copper are claimed, zinc being especially favored.[9] Oxides of aluminum,[10] lead,[11] and magnesium[12] are said to be esterification catalysts; so is a *base exchange material.*[13] Silica gel has been said to be a good catalyst; this has been contradicted. An impartial comparison of these catalysts with hydrochloric acid would be interesting.

Utraviolet light,[14] sound waves,[15] electrical vibrations,[16] and an alternating current[17] have been found to aid in esterifications. An indifferent solvent may influence the reaction. A trace of pyridine was found by one investigator[1] to retard; while others[2] report large amounts of it as being a more effective catalyst than sulfuric acid.[3] Pressure up to 6,500 atmos. does not change the limit with acetic acid and alcohol but does increase the rate.[4]

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[1] Bun-iti Toi, *J. Chem. Soc. Japan*, **61,** 1279 (1940).

[2] Nieuwland *et al.*, *J. Am. Chem. Soc.*, **57,** 1549 (1935); **58,** 271, 786 (1936); Toole and Sowa, *J. Am. Chem. Soc.*, **59,** 1971 (1937); Hennion and Vogt, *Proc. Indiana Acad. Sci.*, **52,** 125 (1942); Kästner, *Angew. Chem.*, **54,** 273 (1941).

[3] Kroeger, Sowa, and Nieuwland, *Proc. Indiana Acad. Sci.*, **46,** 115 (1937).

[4] Freudenberg and Jakob, *Ber.*, **74,** 1001 (1941).

[5] Senderens and Aboulenc, *Compt. rend.*, **152,** 1671, 1855; **153,** 881 (1911); **155,** 168, 1254 (1912); **158,** 581 (1914); *Ann. chim.*, **18,** 145 (1922).

[6] Vassallo, *Olii minerali, dii grassi colori vernici*, **14,** 9 (1934); Akopyan, *J. Gen. Chem.* (*U.S.S.R.*), **7,** 1687 (1937); **8,** 1763 (1938); Russ., 51,047; Johnston, U. S. 2,257,384 (1941).

[7] Petyunin, *J. Gen. Chem.* (*U.S.S.R.*), **10,** 35 (1940).

[8] Adams, Brit. 310,854; I. G. Farbenindustrie A-G; Fr. 654,535; Brit. 302,411; Ger. 556,658.

[9] Gruber, Fr. 677,711; Haddan, Brit. 183,897.

[10] Mackert, Ger. 486,597; Rumple, Hobson, and Hartman, *Proc. Indiana Acad. Sci.*, **50,** 106 (1940).

[11] Shen and Kuo, *Chem. Abs.*, **31,** 3308 (1937).

[12] Palladina, *Chem. Abs.*, **33,** 9469 (1939).

[13] Jaeger, Brit. 308,582.

[14] Stormer and Ladewig, *Ber.*, **47,** 1803 (1914).

[15] Flosdorf and Chambers, *J. Amer. Chem. Soc.*, **55,** 3051 (1933).

[16] Forjaz, *Compt. rend.*, **197,** 1124 (1933).

[17] Spellmeyer, U. S. 2,047,839.

The most interesting and mysterious catalysts are enzymes, though they are not employed in commercial esterifications. Enzymes are probably responsible for the synthesis and hydrolysis of esters in living organisms. Certain of them, called esterases, cause ester formation *in vitro*. They are sometimes selective in their action on optical isomers.[5]

III. COMPLETING ESTERIFICATION

The practical problem that confronts the chemist in carrying out any reaction is obtaining the largest possible amount of the desired product—as nearly 100 per cent as is possible. The esterfication reaction, as has been stated above,

$$CH_3COOH + HOC_2H_5 \rightleftarrows CH_3COOC_2H_5 + H_2O$$

is reversible; *i.e.*, it comes to a standstill when a certain percentage of ester has been produced. We come back to the dictum learned in qualitative analysis: If a gaseous or insoluble product can be formed in a reaction, it will be formed, and the reaction will go to completion in that direction. The equilibrium

$$\frac{[\text{Ester}] \times [\text{water}]}{[\text{Acid}] \times [\text{alcohol}]} = K$$

fixes the relative amounts of the four substances that can coexist. If by some magic a considerable part of either the ester or the water be removed, the equilibrium will be disturbed, and a readjustment must take place. An additional amount of the acid will react with an equivalent amount of alcohol, producing more water and ester until the equilibrium is again established. A numerical example will make this clear. If a mixture of equivalent amounts of acetic acid and alcohol be allowed to come to equilibrium, the percentages of the four substances present will be represented by the fraction below, taking $K = 4$:

$$\frac{66.7 \times 66.7}{33.3 \times 33.3} = 4$$

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[1] Bailey, *J. Chem. Soc.*, **1928,** 1204, 3256.

[2] Schelsinger and Malkina-Okun, *Ber.*, **60,** 1479 (1927).

[3] Smith and Orton, *J. Chem. Soc.*, **95,** 1060 (1906).

[4] Cohen and Kaiser, *Z. physik. Chem.*, **89,** 338 (1918); Newitt *et al.*, *J. Chem. Soc.*, **1937,** 876; **1938,** 784.

[5] Dietz, *Z. physiol. Chem.*, **52,** 279 (1907); Fabisch, *Biochem. Z.* **234,** 84 (1931); Gottschalk and Neuberg, *Biochem. Z.*, **154,** 292 (1924); Rona and Ammon, *Biochem. Z.*, **217,** 34 (1930), Rona, Ammon, and Werner, *Biochem. Z.*, **221,** 381 (1930); Rona and Mühlbock, *Biochem. Z.*, **223,** 130 (1930); Walle, *Nederland. Tijdschr. Hy. Microbiol. Serol.*, **1,** 71 (1926); Weber, *Biochem. Z.*, **129,** 208 (1922).

Now, suppose that all the water is withdrawn. An amount x of acid must react with an equivalent amount of alcohol to form ester and water. When equilibrium is restored, we shall have

$$\frac{(66.7 + x)(0 + x)}{(33.3 - x)(33.3 - x)} = 4$$

Solving this gives $x = 15.4$, so that the quantities become

$$\frac{82.1 \times 15.4}{17.9 \times 17.9} = 3.95$$

The amount of ester is raised from 66.7 to 82.1 per cent. If the removal of the water is repeated, more and more ester will be produced until it reaches 100 per cent and no acid and no alcohol remain.

Berthelot and Péan de St. Gilles saw this clearly in 1863 and accomplished by a clever experiment what we have imagined. They said:

> It can be demonstrated that the presence of water is the only cause which comes in to limit the combination of an acid with an alcohol. In order to obtain complete saturation, it is sufficient to eliminate the water as it is formed in the progressive action of the acid on the alcohol. This can be realized by operating with a fixed alcohol or a fixed acid, *e.g.*, stearic.

They weighed 0.690 gm. of stearic acid and 0.606 gm. (a 2 per cent excess) of cetyl alcohol into a small tube, closed at one end. This was placed upright in a larger tube containing barium oxide, which was then sealed. The whole was heated 26 hr. at 215°C. The barium oxide took up the water that escaped from the reaction mixture. The product dissolved in alcohol was neutral to litmus, showing that the esterfication was complete. Bellucci passed a slow current of carbon dioxide through a mixture of stearic acid and cetyl alcohol heated to 220°C. and obtained a 95 per cent yield of the ester.[1] The preparation of nitric acid esters, wherein the water of reaction is evaporated in a vacuum, has been claimed.[2]

To complete an esterfication, the water must be removed. If it is eliminated as fast as it is formed, there can be no reversal of the reaction. When, as in the above case, the acid, alcohol, and ester are nonvolatile, this is a simple matter.[3] The mixture of acid and alcohol is heated high enough, usually to around 200°C. or higher, to make the reaction go without a catalyst and to drive out the water. The removal of the water may be hastened by bubbling an inert gas through the mixture or by the application of a vacuum. Glycerides of nonvolatile acids are made in this way. To ensure the complete esterfication of the trivalent glycerol, an excess of the acid is used. This is later got rid of by an alkaline wash. Glycols, polyglycols, and pentaerythritol are similarly esterified.[1] Glycerol may be partially esterified by heating it with less than the equivalent of acid.[2]

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[1] BELLUCCI, *Chem. Ztg.*, **35**, 669 (1911).

[2] Hofwimmer, Brit. 360,394.

[3] Graves, U. S. 2,122,716.

Ester gum, a widely used resin, is made by heating glycerol with rosin. Other rosin esters are similarly obtained from rosin and nonvolatile alcohols or glycols.[3] As abietic acid is a hindered acid, the esterification temperature is high, 275 to 300°C, in order to speed up the reaction.

To esterify a relatively nonvolatile acid with a lower alcohol, as in making methyl or ethyl succinate, a large excess of the alcohol is used and is distilled off during the process. This carries the water over as it is formed, which allows the reaction to go to completion.[4] The alcohols, above methyl, form binaries with water. Making *n*-butyl esters of such acids is particularly easy, since the binary, boiling at 92.5°, separates into two layers, the lower of which contains most of the water. The upper can be run back into the esterification mixture automatically.[5] The same holds for the binaries of the alcohols above butyl. The higher the alcohol the larger the proportion of water that it brings over and the less water the upper layer contains.

To assist the removal of the water, certain liquids which are insoluble in water and distill with it at temperatures below its regular boiling point are frequently added to the esterification mixture. Favorite liquids for this purpose are benzene, toluene, chloroform, ethylene chloride, and carbon tetrachloride.[6] When one of these is present, it goes over with the water or with the water and the ester as a constant-boiling mixture which separates into two layers in the receiver. The nonaqueous layer is returned to the reaction vessel from which it distills, again bringing out more of the water. This can be kept up until there is no more water to bring. The separation and return of this auxiliary liquid can be made automatic. Benzene, ethyl alcohol, and water go over at 64.85°C. in the proportions 74.1:18.5:7.4.[7]

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[1] The Emulsol Corp., Brit. 452,138; Gloor, U. S. 2,198,665; Barrell, *Oil Soap*, **21,** 206 (1944).

[2] Kawai *et al.*, *Chem. Abs.*, **34,** 4598, 5689, 7635 (1940); **35,** 3113 (1941).

[3] Liang, *Chemistry (China)*, **3,** 691 (1936); Thomas, U. S. 2,062,950; Schlaanstine, U. S. 2,331,803; Billing, U. S. 2,327,009; Anderson, U. S. 2,346,409.

[4] Harrington, U. S. 2,147,341; West and Jaeger, U. S. 2,169,012; Smith and Claborn, *Ind. Eng. Chem.*, **32,** 692 (1940); Ustinov and Monakhov, Russ. 58,297.

[5] Liston and Dehn, *J. Am. Chem. Soc.*, **60,** 1264 (1938).

[6] Strunnikov, *Chem. Abs.*, **33,** 5805 (1939); Kvalnes, U. S. 2,091,241; Bannister, U. S. 2,076,111; Coleman and Hadler, U. S. 2,127,660; Meyer and Conklin, U. S. 2,173,124; Buxton and Kapp, *J. Am. Chem. Soc.*, **62,** 986 (1940); Richardson, U. S. 2,251,692.

[7] Fritzweiler and Dietrich, *Z. angew. Chem.*, **45,** 605 (1932).

Passing superheated steam through the mixture agitates it and carries off the water as it is formed.[1]

It is just as effective to distill out the ester.[2] Thus, ethyl nitrite, which boils at 16.4°C., is evolved as a gas when alcohol and nitrous acid are brought together in a strongly acid solution.[3] The reaction is so complete that it may be used for the quantitative determination of nitrous acid.[4]

When both ester and alcohol are volatile and go over with the water, the situation is not so simple, but there are ways of handling it. In 1873, Markownikoff prepared ethyl acetate continuously by adding alcohol and acetic acid to sulfuric acid in a flask kept at 130°C.[5] In 1905, Wade made a careful study of this method and laid the foundation for modern esterfication methods.[6] He found it possible to make this ester continuously, starting with a mixture of alcohol and acetic acid, with some sulfuric acid, heating this until the ester begins to distill out and then adding the mixture of alcohol and acetic acid at such a rate that the volume remains constant. What was particularly important was his discovery that the distillate is a ternary mixture of ethyl acetate, 83.2 per cent; alcohol, 9.0 per cent; and water, 7.8 per cent. He found the boiling point of this ternary to be 70.3°C., whereas pure ethyl acetate boils at 77°C. He found a binary, 69.4 per cent of the ester and 30.6 per cent alcohol, boiling at 71.8°C. and a binary of 8.6 per cent water and 91.4 per cent ester boiling at 70.45°C. The important fact is that the ternary boils lower than any of the constituents or either of the binaries and is what comes out at the top of an efficient column as long as all three of its constituents are present in the still. As this ternary behaves on distillation like a pure substance, some other means of separating its components is required. Wade extracted most of the alcohol from this mixture by washing with water. Roberts, who compared several processes, recommended two volumes of water—less than is used in large operations.[7] When this washed ethyl acetate is distilled, the first thing that goes over is again the ternary—ester, water, and alcohol, boiling at 70.3°C., though owing to the washing out of most of the alcohol there can be only a limited amount of it. This is followed by a binary of the ester with either the water or the alcohol, according to which remained from the ternary; then the boiling point goes up to 77.15°C., and pure dry ethyl acetate is obtained.

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[1] Jordan, U. S. 2,307,794.

[2] Wuyts and Bailleux, *Bull. soc. chim. Belg.*, **29**, 55 (1920).

[3] Fischer, *Z. physik. Chem.*, **65**, 61 (1909).

[4] Fischer and Schmidt, *Z. anorg. allgem. Chem.*, **179**, 332 (1929).

[5] Markownikoff, *Ber.*, **6**, 1177 (1873).

[6] Wade, *J. Chem. Soc.*, **87**, 1656 (1905); *J. Soc. Chem. Ind.*, **24**, 1322 (1905).

[7] Roberts, *J. Soc. Chem. Ind.*, **43**, 295 (1924).

It is evident that this investigation gives a satisfactory method of converting a given amount of acetic acid completely into ethyl acetate. It can also be seen that if the ester is removed as rapidly as it is formed, esterfication must go on even in the presence of a considerable proportion of water. To form the ternary, a small excess of alcohol must be put in.

As an illustration, the case of making ethyl acetate from a dilute solution of acetic acid, such as is obtained by the quick-vinegar process, will be considered. Let us take 100 gm. of 5 per cent acetic acid, which would be 0.083 mole of the acid and 5.28 moles of water. If 5 gm. of alcohol (0.108 mole) be added to this along with a catalyst, when equilibrium is reached there will be an amount x of ester formed.

$$\frac{5.28x}{(0.083 - x)(0.108 - x)} = 4$$

which gives $x = 0.0060$ mole or 0.528 gm. This is all that can be formed if all four substances remain in the mixture. Distillation will remove this along with 0.057 gm. of alcohol and 0.0495 gm. of water as the ternary. As soon as this ester is out of the way, more will be formed. If the ester be distilled out continually, esterification will proceed until the last trace of acetic acid is gone. This will leave a slight amount of alcohol, which may be taken off separately as the binary with water and used in another esterification.

As can be readily seen from the above, the manufacture of ethyl acetate becomes a matter of distillation. Obviously, an efficient column is required with ample capacity to take care of the production without being pushed beyond its proper rate. With proper adjustments of rates of esterfication and distillation, the two can be made to go on simultaneously, giving a continuous process. Actually, the liquor containing acetic acid, with the proper amount of sulfuric acid as a catalyst, is fed into the column at the proper plate where it meets the alcohol. Esterification takes place right on the plates in the column, and the ternary of ester, alcohol, and water comes out at the top continuously. This ternary is washed with water, as Wade suggested, and the ester passed to another column. The dilute alcohol obtained by washing the ternary goes to a still for the recovery of the alcohol, which is returned to make more ester.

For other volatile esters, there are corresponding ternaries and binaries. In general, the ternary of an alcohol, its ester, and water boils slightly lower than the binary of the ester and water. The percentage of water in the ternary increases, and that of the ester decreases with increase in molecular weight of the alcohol, as can be seen from the following data (Table IV), most of which are from Hannotte.[1] Methyl acetate boils 10°C. lower than methyl alcohol, but the boiling points of the alcohols rise less rapidly with increasing molecular weight than do those of the acetates. Furnas and coworkers have studied several systems, and Lecat has included esters in his general investigation of azeotropes.[2] Others have contributed to our knowledge of this important subject.

Graphical methods have been developed by Gay, Mion, and Aumèras for determining the conditions for complete esterfication for various mixtures.[3] Later, these authors gave experimental verification of their theories.[4] A study of the above table will show that operating conditions should be adapted to the particular acid and alcohol. Not only the boiling points of the ternaries and binaries come in for consideration but also the solubilities of the esters and alcohols in water. The percentages of ester, alcohol, and water in the ternaries look quite different when they are put on a molar basis.

TABLE IV.—BOILING POINTS OF ESTERS, ALCOHOLS, THEIR BINARIES, AND TERNARIES WITH WATER, °C.

E = ester, *A* = alcohol, *W* = water

	A B.p.	*E* B.p.	Binary *E-W*		Binary *E-A*		Ternary			
			B.p.	H_2O, %	B.p.	*A* %	B. p.	*E* %	*A* %	*W* %
Propyl formate	97.2	81	71.6	2.3	80.6	9.8	70.8	82	5	13
Butyl formate	117.7	106.9	83.8	16.5	105.8	23.7	83.6	68.7	10	21.3
Isobutyl formate	107.9	98.5	80.4	7.8	97.8	20.6	80.2	76	6.7	17.3
Isoamyl formate	131.6	123.3	90.2	21	123.6	26	89.8	48	19.6	32.4
Methyl acetate	64.6	54.0	.....	....	54	18.5				
Ethyl acetate	78.3	77.1	70.45	8.6	71.8	30.6	70.3	83.2	9	7.8
Propyl acetate	97.2	101.6	82.4	14	94.2	40	82.2	59.5	19.5	21
Butyl acetate	117.7	125.1	90.2	28.7	117.2	47	89.4	35.3	27.4	37.3
Isobutyl acetate	107.9	116.3	87.4	16.6	87.4	16.6	86.8	46.5	23.1	30.4
Amyl acetate	137.8	148	95.2	41	.....	....	94.8	10.5	33.3	56.2
Isoamyl acetate	131.6	139	93.8	36.2	.....	....	93.6	24	31.2	44.8

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[1] HANNOTTE, *Bull. soc. chim. Belg.*, **35**, 86 (1926).

[2] BRUNJES and FURNAS, *Ind. Eng. Chem.*, **27**, 396 (1935); FURNAS and LEIGHTON, *ibid.*, **29**, 709 (1937); LECART, *Ann. soc. sci. Bruxelles*, **55B**, 43, 253 (1935); **56B**, 41 (1935); KIREEV, KLINOV, and GRIGOROVICH, *J. Chem. Ind.* (*Moscow*), **12**, 936 (1935); MUND and HEIM, *Bull. Belg.*, **41**, 349 (1932); SKLYARENKO and BARANAEV, *Z. physik. Chem.*, **A175**, 203 (1935).

[3] GAY, MION, and AUMÉRAS, *Bull. soc. chim.* [4], **39**, 1329 (1926).

[4] *Ibid.*, **41**, 1027 (1927).

TABLE V.—MOLAL COMPOSITION OF TERNARIES

	Weight percentages			Molar ratios		
	Ester	Alc.	Water	Ester	Alc.	Water
Ethyl acetate	83.2	9	7.8	2.18	0.45	1
Butyl acetate	35.3	27.4	37.3	0.147	0.178	1

In the case of ethyl acetate, 2.18 moles of ester come over to 1 of water. Hence, esterification is completed by distilling out the ester. In the butyl acetate ternary, only relatively small amounts of ester and alcohol are required to bring over all the water. If a mixture of 1 mole of acetic acid and 1.178 of dry butyl alcohol is slowly distilled, 1 mole of water should come over, bringing with it 0.147 mole of ester and 0.178 mole of alcohol. Since all the water that can be formed has been withdrawn from the mixture, the reaction must be complete, and 0.853 mole of pure butyl acetate remains in the still pot. Thus, 85 per cent of the calculated amount of ester is obtained pure, and the rest of it as a mixture with the alcohol and water. Water is only slightly soluble in this mixture of butyl acetate and butyl alcohol, so that most of the water in the distillate separates out, bringing with it only a little of the alcohol and ester. For simplicity of calculation, we may suppose that the separation is complete, leaving 0.147 mole of ester and 0.178 mole of alcohol. This can be added to the next batch of a mole of acid and one of butanol, and the esterification and distillation repeated. The ternary from this will contain 0.147 mole of ester and 0.178 mole of the alcohol to the 1 of water, which will leave 1 mole of ester in the still. For simplicity, this has been idealized, and no allowance has been made for impurities and losses in handling or for getting rid of the catalyst.

In practice, the distillate is caught in a vessel from the bottom of which the water runs off and from the top of which the ester-alcohol mixture is continuously returned to the still.[1]

Although, as pointed out by Wade, the principles involved in taking advantage of ternaries and binaries in the manufacture of esters are few and simple, many patents have been taken out on particular applications of these principles and on arrangements of apparatus for carrying out the various processes.[2]

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[1] HULTMAN, DAVIS, and CLARKE, *J. Am. Chem. Soc.*, **43**, 366 (1921).

[2] Arentz, Brit. 246,526; Ayres, U. S. 1,869,837; Backhaus, U. S. 1,400,849; 1,400,850; 1,400,851; 1,400,852; 1,403,224; 1,403,225; 1,425,624; 1,425,625; 1,454,462; 1,454,463; Can. 211,675; 211,676; 217,703; 261,187; Bannister, U. S. 2,029,694; Bue and Clough, U. S. 1,726,945; Edlund, Can. 326,768; Holzverkohlungs-Industrie, Brit. 352,647; Horsley and I. C. I., Brit. 301,523; Fr. 671,238; U. S. 1,700,779; Haner, U. S. 1,827,653; Graves, U. S. 1,869,193; I. G. Farben., Fr. 671.123;

On account of the low boiling points of the ternaries involving the lower alcohols and esters, the refluxing temperatures of the esterification mixtures are rather low for rapid reaction unless undesirably large amounts of catalysts are used. This is true also when benzene or another low-boiling liquid is added to carry off the water. Putting an additional atmosphere of pressure on the whole system raises the refluxing temperature something like 20°C. This should quadruple the rate of esterification. Still higher pressures speed it up even more.[1] Changing the pressure alters the composition of the binaries and ternaries somewhat, but they can still be employed in the same way for separations.[2]

It has been proposed to cause the separation of the ester by mixing with a high-boiling mineral oil, from which it may be removed subsequently.[3]

In case a salt of an acid is more available than the free acid, an ester can be made from it directly by adding the desired alcohol together with sufficient sulfuric acid to liberate the organic acid and a little more to serve as a catalyst.[4]

IV. VAPOR-PHASE ESTERIFICATION

In 1863, Berthelot and Péan de St. Gilles, in the course of their study of esterification, tried the effect of changing the volume of the container, keeping the amount of the acid and alcohol constant. The samples were heated 22 hr. at 200°. When the volume was 5 cc. for 1 gm. of mixture, the limit reached was 66.4 per cent, but, when they increased the volume to 25 and 62 cc., the limit went up to 72.9 and 78.4. With very large volume, the esterification was extremely slow, only 49 per cent in 458 hr. These results have been overlooked.

Recently, it has been realized that esterification is quite different in the gas phase from what it is in the liquid.[5] Without a catalyst, it does not seem to take place at all, and, even with the best catalysts, it is so slow that the equilibrium is difficult to determine accurately. This

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685,433; Brit. 307,471; 332,267; Invention Gesellschaft, Brit. 387,573; Marks, Brit. 147,337; Soc. anon. des distilleries des Deux-Sèvres, Brit. 234,458; Standard Oil Devel. Co. Brit. 300,418; 305,308; U. S. Ind. Alc. Co., Brit. 130,968; 130,969; 130,970; 195,117; 195,118; 195,177; 287,607.

[1] Fuchs, Brit. 320,113; U. S. 1,791,238; Holzverkohlungs-Industrie, Brit. 295,275; Fr. 657,812; Brit. 320,113; Roka and Fuchs, Ger. 507,205; U. S. 1,800,319; Wietzel, U. S. 1,732,392; Ger. 490,250; 491,491.

[2] MERRIMAN, *J. Chem. Soc.*, **103,** 1790, 1801 (1913).

[3] Buc, U. S. 1,651,666; 1,808,155; Mann, U. S. 1,541,430; Standard Oil Devel. Co., Brit. 300,418; 305,308.

[4] Burghart, U. S. 1,426,457; Hartwich, Ger 518,388; Mills, Australian 25,884; Schering-Kahlbaum, Brit. 319,043; Wagner, Ger. 529,135; 546,806

[5] MILLIGAN, CHAPPEL, and REID, *J. Phys. Chem.*, **28,** 872 (1924).

explains the widely divergent results that have been reported.[1] Silica gel, metal oxides, and salts are catalysts.[2] Although in the liquid phase the esterification limit is practically the same at 20 and at 200°, it changes markedly with temperature in the gas phase, 85 per cent at 150° and only 75 per cent at 300°. The values of K that correspond to these are 30 and 8.8.[3] K is 122 at 40°.[4]

V. ALCOHOLYSIS

The Esterification of an Ester

$$CH_3COOC_2H_5 + HOCH_3 \rightarrow CH_3COOCH_3 + HOC_2H_5 \qquad (4)$$

The reaction [(4), above] is spoken of as *alcoholysis* and also as ester interchange or reesterification. It is making an ester by the reaction of an alcohol with an ester instead of an acid. An example of it was observed by Guthrie in 1859, but it was a long time before its generality was recognized.[5] It has been discovered more times than probably any other reaction, since many of those observing a case of it have investigated it as new.

If a mixture of amyl nitrite and ethyl alcohol containing some acid is warmed, ethyl nitrite distills out. Friedel and Crafts heated ethyl acetate with amyl alcohol and amyl acetate with ethyl alcohol and observed alcoholysis in both cases.[6] They even heated ethyl benzoate and amyl acetate together and got ethyl acetate and amyl benzoate, though they found this reaction to be slow below 300°C.

Alcoholysis is only a special case of esterification; it comes under the same rule that applies to other cases. If benzoic acid is heated with a mixture of methyl and ethyl alcohols, we have the equilibriums:

$$[\text{Me Benzoate}] \times [H_2O] = [\text{Benzoic Acid}] \times [\text{MeOH}] \cdot K_1$$
$$[\text{Et Benzoate}] \times [H_2O] = [\text{Benzoic Acid}] \times [\text{EtOH}] \cdot K_2$$

Dividing one of these by the other, we have

$$\frac{[\text{Me Benzoate}] \times [\text{EtOH}]}{[\text{Et Benzoate}] \times [\text{MeOH}]} = \frac{K_1}{K_2} = K$$

This holds in the absence as well as in the presence of the water and free acid.[7] Thus the alcoholysis equilibrium can be calculated from the esterification constants of the two alcohols severally with benzoic acid:

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[1] Frolich, Carpenter, and Knox, *J. Am. Chem. Soc.*, **52,** 1565 (1930); Edgar and Schuyler, *J. Am. Chem. Soc.*, **46,** 64 (1924); Essex and Clark, *J. Am. Chem. Soc.*, **54,** 1290 (1932); Jatkar and Gajendragad, *J. Am. Chem. Soc.*, **59,** 798 (1937).

[2] Vernon, *Ind. Eng. Chem.*, **32,** 534 (1940); Whitacre and Briscoe, *Proc. Indiana Acad. Sci.*, **46,** 133 (1937); *C.A.*, **32,** 492.

[3] Tidwell and Reid, *J. Am. Chem. Soc.*, **53,** 4353 (1931).

[4] Halford and Brundage, *J. Am. Chem. Soc.*, **64,** 36 (1942).

[5] Guthrie, *J. Chem. Soc.*, **11,** 245 (1859).

[6] Friedel and Crafts, *Ann.* **130,** 198 (1864); **133,** 207 (1865).

[7] Reid, *Am. Chem. J.*, **45,** 479 (1911); Bruni, *Chem. Ztg.*, **35,** 614(1911).

$$K = \frac{K_1}{K_2} = \frac{5.237}{3.968} = 1.32$$

This means that if 1 mole of methanol is added to 1 mole of ethyl benzoate, 53.5 per cent of the methyl ester will be formed and a like amount of ethyl alcohol set free. At room temperature, in the absence of a catalyst, a long time would be required for the establishment of the equilibrium. As this reaction is a variety of esterification, it should be accelerated by esterification catalysts—and so it is. The strong acids that are used in ordinary esterification serve equally well for alcoholysis.[1] The most commonly used catalysts are of an entirely different sort, sodium alcoholates.[2] These must be used in anhydrous systems since they are hydrolyzed by water and disappear in the hydrolysis of esters. The usual practice is to dissolve a small amount of sodium in the alcohol that is to be used and then add the ester. Small concentrations of these catalysts cause the transformation to take place rapidly even at room temperature.

The remarkable quality of alcoholysis is its rapidity, at least with sodium alcoholate as a catalyst, as compared with esterification and saponification. The saponification of phenyl benzoate in aqueous alcohol would ordinarily be represented by (*b*):

$$C_6H_5COOC_6H_5 + NaOC_2H_5 = C_6H_5COOC_2H_5 + C_6H_5ONa \qquad (a)$$
$$C_6H_5COOC_6H_5 + NaOH \rightarrow C_6H_5COONa + C_6H_5OH \qquad (b)$$

What actually takes place is the alcoholysis as represented in (*a*), which was estimated by Gibby and Waters as one thousand times as rapid as the saponification according to (*b*).[3] Then the ethyl benzoate is slowly saponified. This may be shown qualitatively by a simple experiment. Some triacetin [$C_3H_4(OCOCH_3)_3$], which is odorless, is added to a solution of caustic soda in 50 per cent alcohol; the odor of ethyl acetate is apparent at once, showing that the immediate reaction is the formation of ethyl acetate. On this account, it is necessary to use an efficient reflux condenser when determining saponification numbers of even high-boiling acetates.[4]

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[1] Röse, *Ann.*, **205**, 240 (1880); Lel'chuk and Popova, *Org. Chem. Ind.* (*U.S.S.R.*), **3**, 148 (1937); **5**, 628 (1938); Varvogalis, *Ber.*, **71**, 2488 (1938); Flory, *J. Am. Chem Soc.*, **62**, 2261 (1940).

[2] Purdie, *J. Chem. Soc.*, **47**, 855 (1885); **51**, 627 (1887); *Ber.*, **20**, 1555 (1887) Purdie and Marshall, *J. Chem. Soc.*, **53**, 391 (1888); Sudborough and Karvé *J. Indian Inst. Sci.*, **3**, 1 (1919); **5**, 1 (1922).

[3] Gibby and Waters, *J. Chem. Soc.*, **1932**, 2643.

[4] Béhal, *Bull. soc. chim.* [4], **15**, 565 (1914); Hasche, Pardee, and Reid, *Ind Eng. Chem.*, **12**, 129, 481 (1920); Pinnow, *Z. Elektrochem.*, **24**, 270 (1918).

Besides the sodium alcoholates, various other catalysts for this reaction have been recommended: ammonia, pyridine,[1] aluminum alkoxides, $Al(OR)_3$,[2] ROMgBr,[3] sodium phenoxides,[4] potassium carbonate,[5] calcium and lead oxides,[6] and metals—copper, nickel,[7] tin, and zinc[8]—also calcium naphthenate.[9]

Since, as mentioned above, the alcoholysis equilibrium depends on the esterification constants of the two alcohols, a tertiary alcohol even in large excess would not be expected to replace a primary, and only a small yield is obtained with a secondary.[10] The relative activity of the alcohols has been measured.[11]

An interesting case is the preparation of the monomeric cyclic polymethylene carbonates which can be obtained in no other way. A higher polymethylene glycol and sodium are heated with butyl carbonate to obtain the polymeric polymethylene carbonate. This, still containing the catalyst, is heated in a high vacuum; the trace of monomeric cyclic ester x that is present distills out, and more is formed by rearrangement until nearly all the material is obtained in the desired form.[12]

Completing Alcoholysis.—The situation here is just the same as was discussed above in esterification; the removal of one of the reaction products permits the reaction to go to completion. Thus, a higher alcohol such as butyl, amyl, or benzyl is added to methyl or ethyl acetate with a catalyst, and the mixture heated under a fractionating column. The most volatile thing present is the methyl or ethyl alcohol, which distills out, leaving the ester of the other alcohol.[13] Or the new ester may distill off, as when ethyl alcohol reacts with glycol acetate.

When a glyceride is alcoholized by an alcohol, such as ethyl, the glycerol separates out on account of its low solubility in esters, allowing the reaction to go far toward completion. It is washed out with water, and the alcoholysis repeated if necessary.

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[1] Weddige, *J. prakt. Chem.* [2], **12,** 434 (1895).

[2] Calingaert, Soroos, Hnizda, and Shapiro, *J. Am. Chem. Soc.*, **62,** 1545 (1940); Sorenson, U. S. 2,251,765; Fein, Ratchford, and Fisher, *J. Am. Chem. Soc.*, **66,** 1201 (1944); Du Pont Co., Brit. 552,228.

[3] Frank, Davis, Drake, and McPherson, *J. Am. Chem. Soc.*, **66,** 1509 (1944).

[4] Kinzerskaya, *J. Appl. Chem.* (*U.S.S.R.*), **10,** 1889 (1937).

[5] Loder and Teeters, U. S. 2,290,128.

[6] Blagonravova, Antipova, Savvina, and Svetlichnaya, *J. Appl. Chem.* (*U.S.S.R.*), **14,** 192 (1941).

[7] Berner and Hjulstad, *Ber.*, **71,** 2052 (1938).

[8] Kawai and Yamamoto, *Chem. Abs.*, **35,** 1255, 3113 (1941).

[9] Burrell, U. S. 2,360,393.

[10] Reimer and Downes, *J. Am. Chem. Soc.*, **43,** 945 (1921).

[11] Kolhatkar, *J. Chem. Soc.*, **107,** 921 (1915); Fehlandt and Adkins, *J. Am. Chem. Soc.*, **57,** 193 (1935); Hatch and Adkins, *J. Am. Chem. Soc.*, **59,** 1694 (1937).

[12] Carothers and associates, *J. Am. Chem. Soc.*, **55,** 5031 (1933); **57,** 929 (1935); U. S. 2,020,298; Brit. 433,632; Fr. 768,807; 796,410.

[13] Adickes, Plessmann, and Schmidt, *Ber.*, **70,** 2119 (1937); Du Pont and Woodhouse, Brit. 461,979; Röhm and Haas, Brit. 520,164; Kautter, Ger. 706,792; Loder, U. S. 2,290,128.

The modification of drying oils by partial or complete alcoholysis is becoming more and more important.[1]

Equipment and Operation for Alcoholysis.—As only anhydrous esters and alcohols and an alkaline catalyst, none of which causes corrosion, are used, the equipment may be of the simplest sort; a kettle and a column with suitable attachments suffice. Usually, the alcohol is put in the kettle first, and the sodium metal (0.1 to 1 per cent of the weight of the ester) introduced. The ester is run in; the heat turned on; and distillation begun.

VI. ACIDOLYSIS

$$CH_3COOC_2H_5 + C_{15}H_{31}COOH \leftrightharpoons C_{15}H_{31}COOC_2H_5 + CH_3COOH$$

The counterpart of alcoholysis—acidolysis—in which one acid displaces another from its ester [reaction (5)] is so similar to alcoholysis that little need be said about it. As the alkaline catalysts that are so efficient in alcoholysis can not be used, reliance has to be put on the slower acid catalysts or on heat alone. Boron fluoride is effective.[2] Mercury salts[3] are recommended for vinyl esters. Quantitative studies show that one acid displaces another to about the extent that would be expected from the esterification constants.[4] The reaction goes to completion if the displaced acid can be eliminated. Volatile acids can be distilled out, either as such or as azeotropes.[5] A phenol can be esterified by heating it with a nonvolatile acid and acetanhydride. Presumably, the acetate is formed, and then the acetic acid is displaced.[6]

VII. ESTERIFICATION OF AMIDES

An excellent way to make an acid amide is to treat an ester with ammonia:

$$CH_3COOC_2H_5 + NH_3 \leftrightharpoons CH_3CONH_2 + HOC_2H_5$$

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[1] ECKMANN, *Farben-Chem.*, **12,** 34, 39, 63 (1941); WRIGHT, *et al.*, *Oil Soap*, **21,** 145 (1944); Alexander Wacker Ges., Ger. 642,454; Robinson, U. S. 2,123,206; Hansley, U. S. 2,177,407; Gooding, U. S. 2,309,940; Loder and Teeters, U. S. 2,350,964; Johnston, Can. 420,054.

[2] SOWA, *J. Am. Chem. Soc.*, **60,** 654 (1938).

[3] Herrmann and Haehnel, U. S. 2,245,131; Toussaint and MacDowell, U. S. 2,299,862.

[4] CHERBULIEZ and FULD, *Chem. Abs.*, **33,** 3241 (1939); TOYAMA, *Chem. Abs.*, **33,** 8569 (1939); GAULT and CHABLAY, *Compt. rend.*, **207,** 293 (1938); BARKENBUS, *J. Am. Chem. Soc.*, **62,** 1251 (1940).

[5] Labert Products, Ltd., Brit. 486,341; Coleman and Schroeder, U. S. 2,363,501; de Ropp, U. S. 2,162,451; Cherry, U. S. 2,082,790; 2,212,509.

[6] COLEMAN and SCHROEDER, U. S. 2,363,501.

Though the reaction is reversible [reaction (7)], the yield of the amide is almost quantitative, since the equilibrium is far over to that side. However, it is easy to convert an amide completely into the ester by the addition of an excess of an acid such as sulfuric or hydrochloric which combines with the ammonia. When a high-boiling alcohol is used, the ammonia can be driven off by heating. This reaction has been studied by several investigators, and there are a few patents on its applications.[1,2] It has been found useful for making dithio-esters.[3]

VIII. USE OF ACID ANHYDRIDE

Reactions (8), (9), and (10) go to completion, since the acid that is formed cannot decompose the ester.

$$(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH \tag{8}$$

$$(CH_3CO)_2O + (CH_3)_3COH \rightarrow CH_3COOC(CH_3)_3 + CH_3COOH \tag{9}$$

$$(CH_3CO)_2O + C_6H_5ONa \rightarrow CH_3COOC_6H_5 + CH_3COONa \tag{10}$$

Furthermore, acetic anhydride reacts more rapidly with a given alcohol than does acetic acid under the same conditions, though the relative velocities with different alcohols as measured by Menschutkin are much the same.[4] This discussion will be limited to acetic anhydride, the cheapest anhydride of a monobasic acid and the one commonly used.

The simpler primary and secondary alcohols can be satisfactorily esterified by the methods already described, but certain tertiary alcohols, mercaptans, and phenols require the use of acetic anhydride. It is frequently used for small lots of expensive alcohols in cases where speed and completeness of esterification are of more importance than the added cost of the anhydride.

The usual method is to boil the alcohol and an excess of acetic anhydride with 10 per cent of anhydrous sodium acetate for several hours. The sodium acetate speeds up the reaction somewhat. The product is cooled and agitated with warm water, which hydrolyzes the remaining acetic anhydride and dissolves out the acetic acid. The acetate is separated and washed several times with water and finally with weak soda until it is neutral.

Reactions with acetic anhydride are greatly accelerated by sulfuric

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[1] Magill, *Ind. Eng. Chem.*, **26**, 611 (1934); Reid, *Am. Chem. J.*, **41**, 483 (1909); Taylor and Davis, *J. Phys. Chem.*, **32**, 1467 (1928).

[2] Gibson and Payman, Brit. 307,137; Ger. 523,189; U. S. 1,877,847; Nieuwland and Sowa, U. S. 2,036,353; Smith, Fr. 665,162; Brit. 313,316; Trusler, U. S. 1,584,907; Brit. 255,887.

[3] Reid, *Orig. Com. 8th Intern. Congr. Appl. Chem.* (Appendix), **25**, 423.

[4] Menschutkin, *Ann.*, **195**, 334 (1879); **197**, 193 (1879); *Ber.*, **13**, 162 (1880); *Ann. chim.* (5), **23**, 14 (1881); **30**, 81 (1883); *Z. physik. Chem.*, **1**, 611 (1887); **9**, 237 (1892).

acid, zinc chloride, phosphorus pentoxide, ferric chloride, etc.,[1] but such catalysts cannot be used with sensitive alcohols, like linalool, which are isomerized or otherwise affected by them. An aromatic anhydride may be made to react by the addition of caustic soda.[2] A tertiary base may be used to assist esterifications by acid anhydrides.[3]

IX. USE OF ACID CHLORIDES

$$C_2H_5OH + ClCOCl \rightarrow C_2H_5OCOCl + HCl \qquad (11)$$

$$C_2H_5OH + C_2H_5OCOCl \rightarrow (C_2H_5O)_2CO + HCl \qquad (12)$$

$$3C_2H_5ONa + Cl_3PO \rightarrow (C_2H_5O)_3PO + 3NaCl \qquad (13)$$

$$C_6H_5ONa + CH_3COCl \rightarrow C_6H_5OCOCH_3 + NaCl \qquad (14)$$

Reactions (11), (12), (13), and (14) involve the use of an acid chloride and result in the formation of hydrogen chloride or sodium chloride. The remarks that were made about acid anhydrides might be repeated with little change about acid chlorides. The latter are much more reactive and are, in general, easier to prepare. Hence, they are widely used, particularly in the laboratory. The disadvantages are that the hydrogen chloride evolved may cause changes in the organic compounds or corrosion of metal equipment.

For making alkyl carbonates, phosgene ($COCl_2$), the acid chloride must be used, since carbonic acid is not available and its anhydride does not react with alcohols. The making of a dialkyl carbonate is simple; the phosgene is led into an excess of the cold alcohol. The first stage, reaction (11), goes rapidly at room temperature or below. The second reaction (12) is much slower and is completed by long standing or by heating. If the acid ester, ROCOCl, is desired, the alcohol is added to cold, liquid phosgene, the excess of which is later evaporated off. The second stage may be aided by the addition of a tertiary amine, such as pyridine or dimethylaniline;[4] a weak base;[5] or even cold sodium hydroxide.[6] This is necessary in case the second alcohol is different from the first, as in making RO·CO·OR′.

There is a great deal of difference in the reactivity of different acid chlorides; those derived from aromatic acids react much more slowly than aliphatic, and arylsulfonyl chlorides are still slower. Thus, benzoyl chloride dissolved in an excess of ethyl alcohol and kept at 0°C. requires 4 hr. for complete reaction, but acetyl chloride reacts practically instantly.[1] To speed up the reaction of a sluggish acid chloride, the mixture is sometimes heated, or the Schotten-Baumann method is used [reaction (14)]; *i.e.*, the alcohol or phenol is mixed with 10 or even 25 per cent caustic soda solution, and the acid chloride is added slowly with vigorous agitation, while the temperature of the mixture is kept down to 0°C. or below.[2] Instead of the aqueous alkali, anhydrous tertiary bases may be used.[3] The reactants are mixed cold, but the mixture may be heated later.

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[1] KNOEVENAGEL, *Ann.*, **402,** 111 (1914); SWANSON and COSS, *Chem. Abs.*, **33,** 7731 (1939); NAZAROV, Russ. 57,134; BAKER and BORDWELL, *Org. Syntheses*, **24,** 18 (1944); CIUSA and SOLLAZZO, *Chem. Abs.*, **38,** 5794 (1944).

[2] AUTENREITH and THOMAE, *Ber.*, **57,** 1002 (1924).

[3] Malm and Fordyce, U. S. 2,023,485; LÉMAN, *Compt. rend.*, **210,** 78 (1940).

[4] Schwing, Fr. 650,100; 34,412 (1927).

[5] KREMANN, *Monatsh.*, **29,** 23 (1908).

[6] DRAKE and CARTER, *J. Am. Chem. Soc.*, **52,** 3720 (1930); Grether, U. S. 1,877,304; 1,877,305.

The reaction of an acid chloride with a phenol is facilitated by aluminum chloride.[4] The yields of esters from phenols and tertiary alcohols are high when magnesium is present.[5] Liquid sulfur dioxide is a suitable medium in which to carry on the reaction.[6]

One case demands special attention on account of the desirability of some of the products, and that is the synthesis of trialkyl or triaryl phosphates as represented by reaction (13). Phosphorus oxychloride is made to react with an alcohol or with mixtures of alcohols or, more commonly, phenol, cresols, or mixtures of these. The reactants are brought together at room temperature or below but may be heated later. The hydrogen chloride may be removed by a current of air or taken care of by the addition of alkali.[7]

X. ESTERS FROM METAL SALT AND ALKYL HALIDE

Heating a metal salt of an acid with an alkyl halide [reactions (15) and (16)] substitutes the alkyl for the metal, thus forming an ester.

$$CH_3COONa + BrC_2H_5 \rightarrow CH_3COOC_2H_5 + NaBr \qquad (15)$$

$$CH_3COONa + ClCH_2C_6H_5 \rightarrow CH_3COOCH_2C_6H_5 + NaCl \qquad (16)$$

---

[1] Reid, Unpublished.

[2] Baumann, *Ber.*, **19**, 3218 (1886); Schotten, *Ber.*, **17**, 2545 (1884); **23**, 3430 (1890).

[3] Palomaa, Salmi, Jansson, and Salo, *Ber.*, **68**, 303 (1935); Sabetay, *Bull. soc. chim.* [4], **47**, 436 (1930); Stimmel and King, *J. Am. Chem. Soc.*, **56**, 1724 (1934); Suzuki and Kaisha, Jap. 38,647; Abramovitch, Shivers, Hudson, and Hauser, *J. Am. Chem. Soc.*, **65**, 986 (1943); Clark and Brauns, *Paper Trade J.*, **119**, No. 6, 33 (1944); Heim and Poe, *J. Org. Chem.*, **9**, 299 (1944).

[4] Ross, U. S. 2,345,006.

[5] Spassow, *Ber.*, **70**, 1926 (1937); **75**, 779 (1942).

[6] Ross, *et al.*, *Ind. Eng. Chem.*, **34**, 924 (1942); Colgate-Palmolive-Peet, Brit. 532,685.

[7] Bass, U. S. 2,071,323; Bryner, U. S. 1,856,862; Chem. Fab. Griesheim Elektron, Brit. 181,835; Evans, Davies, and Jones, *J. Chem. Soc.*, **1930**, 1310; Hand and Magoun, U. S. 1,866,852; I. G. Farben., Brit. 291,773; Ger. 478,127; 523,802; 531,213; Fr. 664,770; 668,686; Laska and Prillwitz, U. S. 1,425,392; 1,425,393; Nicolai, U. S. 1,844,408; Nicolai, Schoenburg, and Bruck, U. S. 1,869,768.

This reaction is frequently used for preparing esters,[1] especially those which may identify the acids.[2] For this purpose, we choose the halide of a radical that is likely to give a crystalline ester. Silver salts, which are readily prepared from acids, are frequently employed for this purpose, since no solvent is required and the resulting esters need little purification. Thallium salts are said to give particularly good yields of esters. For manufacturing purposes, this reaction is useful in a few cases only—those in which the alkyl halide is cheaper than the corresponding alcohol or in which the ester is difficult to obtain by direct esterification. The best known case is that of the manufacture of benzyl acetate from sodium acetate and benzyl chloride.[3] As the benzyl chloride is made by chlorinating toluene, it is the most available benzyl compound. The two reactants are brought together in a mutual solvent, which may be acetic acid or aqueous alcohol, and the mixture is heated until the benzyl chloride is used up, which is apparent by the disappearance of the sharp odor. The *p*-nitrobenzyl ester is made similarly.[4] Amyl chloride, from the chlorination of pentane, is used for the large-scale manufacture of amyl acetate.[5]

Dialkyl phthalates in which the two alkyls may be the same or different are prepared by heating a sodium mono-alkyl phthalate with an alkyl halide.[6]

Various compounds, particularly amines, are claimed as catalysts.[7] An excellent yield of benzyl benzoate can be obtained by heating dry sodium benzoate with benzyl chloride and 1 per cent of a tertiary amine.[8]

Since reactions of this type are slow, except at temperatures above 100°C., they are usually carried out in autoclaves to avoid loss of volatile materials. When the reaction is complete, the autoclave is cooled and the charge drowned in water. The ester is separated, washed free of salts, dried, and rectified.

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[1] Consortium für Elektrochem. Ind., Fr. 465,965; Ger. 277,187; 277,188; Brit. 26,825; 26,826 (1913); Ger. 277,111; 285,990; 286,812; Brit. 4,887 (1915); Swiss 74,445; Norw. 30,419; 30,906; Dykstra, U. S. 2,072,739; Nicholl, U. S. 1,984,982; Shering-Kahlbaum A-G., Ger. 592,131; Coleman and Moore, U. S. 2,021,852.

[2] Reid, *J. Am. Chem. Soc.*, **39,** 124 (1917); Judefind and Reid, *ibid.*, **42,** 1043 (1920); Lyons and Reid, *ibid.*, **39,** 1727 (1917); Rather and Reid, *ibid.*, **41,** 75 (1919); Moses and Reid, *ibid.*, **54,** 2101 (1932).

[3] Béhal, *Compt. rend.*, **147,** 1478 (1908); Hefti and Schilt, Brit. 229,958.

[4] Hartman and Rahrs, *Org. Syntheses*, **24,** 81 (1944).

[5] Ayres, U. S. 1,869,837; Ayres and Haabestad, U. S. 1,691,425.

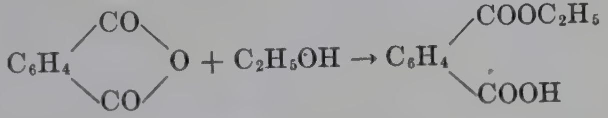
[6] Dykstra, U. S. 2,072,739; Kyrides, U. S. 2,073,937; Pollack and Chenicek, U. S. 2,275,467.

[7] Coleman and Moore, U. S. 2,021,852; 2,115,905; Givaudan and Cie, Swiss 169,040; Lawson, U. S. 2,049,207.

[8] Badische, Ger. 268,621.

XI. ESTERS FROM ANHYDRIDES OF DIBASIC ACIDS

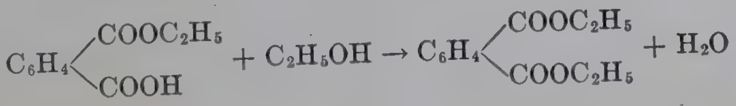
Monoalkyl phthalates are obtained with great ease by heating phthalic anhydride with an alcohol [reaction (17)]



$$C_6H_4\left\langle{CO \atop CO}\right\rangle O + C_2H_5OH \rightarrow C_6H_4\left\langle{COOC_2H_5 \atop COOH}\right. \qquad (17)$$

The speed of this reaction is dependent on the nature of the alcohol. Advantage is taken of this fact to separate alcohols of the various classes; primary alcohols diluted with benzene are supposed to react completely with phthalic anhydride at 80° in an hour, whereas secondary have to be heated to 130 to 140°C. for several hours. Tertiary alcohols are dehydrated before they combine. The phthalic anhydride and one equivalent of the alcohol are heated until combination takes place, usually at 130°, the melting point of the anhydride. The monoalkyl phthalate so obtained may be freed from any uncombined alcohol by a quick steam distillation; from unreacted phthalic anhydride or acid, by solution in ether or benzene; from dialkyl ester, by solution in sodium carbonate or caustic soda. To form the sodium salt, the exact amount of alkali must be added to the monoalkyl phthalate, since the sodium alkyl phthalate is readily salted out by an excess of alkali. The monoalkyl phthalate may be precipitated from the purified solution of its sodium salt.

Heating the monoalkyl ester with an excess of the alcohol gives the dialkyl ester, but this reaction is slow and requires either a high temperature or a catalyst.



$$C_6H_4\left\langle{COOC_2H_5 \atop COOH}\right. + C_2H_5OH \rightarrow C_6H_4\left\langle{COOC_2H_5 \atop COOC_2H_5}\right. + H_2O$$

Esters from Dibasic Acids and Polyhydric Alcohols.—Polymeric esters which may serve as resins are obtained when dihydric alcohols are heated with dibasic acids. As two or more glycols may be used with two or more acids and in various proportions, a great variety of products can be prepared.[1]

The reaction of phthalic anhydride with glycerol has been of particular interest.[2] The product, called Glyptal, was the first of the alkyd resins which are now manufactured in enormous quantities. These are complex mixtures produced by heating polyvalent alcohols with dibasic acids, with the addition of more or less of monobasic acids. The sum of the equivalents of acids is approximately equal to that of the alcohols. It is desirable that the acid number of the final product be as low as possible. The chief alcohol is glycerol; others are glycol, pentaerythritol, mannitol, and sorbitol. Phthalic is the main dibasic acid; others are maleic, sebacic, and adipic. The monobasic acid is usually one of the higher ones. Instead of pure individual acids, it is common practice to use the crude acid mixtures that are obtained by saponifying natural oils such as linseed, castor, soybean, cottonseed, and coconut. These materials are proportioned so as to give the desired physical characteristics.

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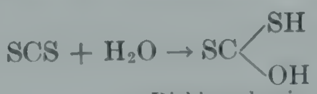
[1] Sly, U. S. 2,073,031; Cox and Carruthers, U. S. 2,106,703; Petrov, Andrianov, and Dzhenchel'skya, *Chem. Abs.*, **33**, 5088 (1939); Blagonravova and Lazarev, *Chem. Abs.*, **35**, 2060 (1941).

[2] Kienle, Van der Meulen, and Petke, *J. Am. Chem. Soc.*, **61**, 2258, 2268 (1930). Al'tman and Kedrinskii, *Chem. Abs.*, **31**, 6219 (1937).

XII. XANTHATES

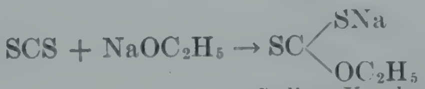
Carbon disulfide may be regarded as the anhydride of a dibasic acid:



$$SCS + H_2O \rightarrow SC\begin{cases} SH \\ OH \end{cases}$$

Dithiocarbonic Acid

This reaction does not take place, but carbon disulfide does combine readily with a sodium alcoholate, as in reaction (18).



$$SCS + NaOC_2H_5 \rightarrow SC\begin{cases} SNa \\ OC_2H_5 \end{cases}$$

Sodium Xanthate

The product is the sodium salt of the monoalkyl ester of the above acid. The reaction is readily carried out: Metallic sodium is dissolved in the anhydrous alcohol, or caustic alkali is mixed with the alcohol, which may contain some water, and carbon disulfide is added.[1] The union takes place at room temperature, and the sodium or potassium xanthate may be purified by recrystallization.

Cellulose xanthate, which is made in enormous quantities—tens of thousands of tons annually—as an intermediate in the manufacture of rayon and Cellophane, will be taken up in a later section.

XIII. ESTERIFICATION BY KETENE

There has been much interest in ketene as a means of producing esters, since it unites directly with alcohols:[2]

$$CH_2{:}CO + C_2H_5OH \rightarrow CH_3COOC_2H_5 \qquad (21)$$

The reaction is attractive, since all the ketene goes into the product and there are no by-products. In effectiveness, ketene may be considered the equivalent of acetic anhydride. The drawback is the present cost of ketene. Diketene is used for making acetoacetic esters.[1]

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[1] Christmann and Jayne, U. S. 1,810,552; 1,852,110; Hirschkind, U. S. 1,704,249; 1,872,452; Rosenstein, U. S. 1,854,525; 1,872,821.

[2] Morey, *Ind. Eng. Chem.*, **31**, 1129 (1939).

XIV. ADDITION OF AN ACID TO AN UNSATURATED HYDROCARBON

The addition of an organic acid to an unsaturated hydrocarbon is not so simple a matter as is represented by reaction (24).

$$CH_2{:}CH_2 + CH_3COOH \rightarrow CH_3COOC_2H_5 \qquad (24)$$

This reaction does not go well with ethylene but does with many of the higher alkenes, particularly with some of the terpenes. Sulfuric acid,[2] commonly used to effect the union, is spoken of as a catalyst, though it is probable that a mono-alkyl sulfate is formed and that this reacts with the organic acid. To get away from the polymerizing effects of sulfuric acid, various other catalysts such as sulfonic acids,[3] triethylamine,[4] hydrofluoric acid,[5] boron fluoride,[6] and cuprous chloride have been proposed.[7] The addition may take place at room temperature or higher; it is aided by pressure. The vapors of the acid and hydrocarbon may be passed over catalysts, such as activated carbon,[8] heteropoly acids,[9] and metal phosphates.[10] Ethyl phosphate may be mixed with the vapors.[11] Mono-,[12] di-,[13] and tri-chloroacetic[14] acids have been added to unsaturates.

XV. ESTERS FROM ACETYLENE

When acetylene and acetic acid are brought together with a suitable catalyst, union takes place to form a vinyl ester or an ester of ethylidene glycol according to reactions (27) and (28).

$$CH{:}CH + CH_3COOH \rightarrow CH_3COOCH{:}CH_2 \qquad (27)$$
$$CH{:}CH + 2CH_3COOH \rightarrow CH_3CH(OCOCH_3)_2 \qquad (28)$$

[1] Gleason, U. S. 2,180,953; Pohl and Schmidt, Ger. 717,652.

[2] Francis, U. S. 2,079,652; Davis and Francis, U. S. 2,169,227.

[3] Coleman, U. S. 2,224,809.

[4] Hansley, U. S. 342,612.

[5] Simons and Meunier, *J. Am. Chem. Soc.*, **63**, 1921 (1941).

[6] Schneider, U. S. 2,065,540; Dorris and Sowa, *J. Am. Chem. Soc.*, **60**, 358 (1938); Zavgorodnii, *Chem. Abs.*, **33**, 5805 (1939); Nieuwland and Sowa, U. S. 2,192,015; Petrov and Azatyan, *Chem. Abs.*, **35**, 3966 (1941); Loder, U. S. 2,253,525; I. G. Farben., Ger. 728,530.

[7] Gilliland, U. S. 2,310,283.

[8] Larson, U. S. 2,093,695.

[9] Lazier, U. S. 2,174,985.

[10] The Distillers Co., Brit. 541,056.

[11] Dreyfus, U. S. 2,217,735; Brit. 485,108.

[12] Aldoshin, *Chem. Abs.*, **33**, 4194 (1939); Borglin, U. S. 2,217,611; 2,227,059; 2,227,061; 2,239,459; 2,275,606.

[13] Arundale and Mikeska, U. S. 2,307,872.

[14] Scovill, *J. Am. Chem. Soc.*, **66**, 1039 (1944).

The one reaction or the other may be favored by changing conditions.[1] Vinyl and ethylidene acetates are produced on a large scale. The reaction goes with other acids and with acetylene derivatives. The usual catalysts are strong acids, sulfuric, methane di- and tri-sulfonic and phosphoric, with or without mercury salts. Boron fluoride has been claimed, as are salts of other metals.[2] The addition may be effected in the vapor phase; the acid and acetylene are passed over a solid catalyst at 200° or above.[3]

XVI. ESTERS FROM NITRILES

$$CH_3CN + H_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + NH_3 \tag{29}$$

This reaction (29) is of importance for the reason that the nitriles are intermediate steps in the synthesis of certain acids. If the ester is wanted, it saves one operation to make it directly from the nitrile instead of saponifying the nitrile and then esterifying the acid in the usual way. The nitriles of hydroxy acids, in particular, are readily obtained by the addition of hydrocyanic acid to an aldehyde:

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

The esterification of the nitrile presents no great difficulty. Enough acid must be used to combine with the ammonia that is formed and more to act as catalyst. A higher temperature and longer time are required than for simple esterification. Sulfuric acid is the usual catalyst, but hydrochloric acid may be employed, and zinc chloride may be added. The equipment is the same as for esterification, and the purification of the esters is the same. The amount of water may be kept low, but a considerable excess of alcohol is used, so that the ester has to be separated from the alcohol. As the esters prepared in this way are usually high boiling (ethyl lactate boils at 154°C.), the alcohol and water are distilled off from the ester. An inert solvent in which the ammonium salt is insoluble is frequently added to take up the ester. After the ammonium salt is filtered off, the solution of the ester may be washed with water, separated, and fractionated.[4]

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[1] Morrison and Shaw, *Trans. Electrochem. Soc.*, **63,** 23 (1933).

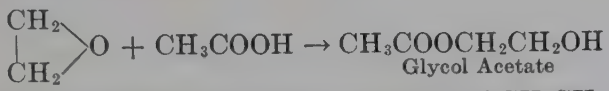
[2] I. G. Farben., Fr. 819,395; Yamada, *Chem. Abs.*, **32,** 6229 (1938); Boehringer and Söhne, Ger. 643,800, 692,354; Dinwiddie, U. S. 2,254,212; DuPont, Brit. 539,235; Rabald, Ger. 692,354; Morrison, *Chem. Ind.*, **1941,** 387; Brown and Watt, Brit. 512,806; Reppe and Wolff, Ger. 722,465; Deut. Gold u. Silber Scheide An., U. S. 2,191,053; Cockerille, U. S. 2,351,664; Carbide and Chemical Co., Fr. 827,757; Toussaint, Brit. 490,334; Wolfram and Jahn, U. S. 2,339,126; Lange and Dorrer, U. S. 2,156,093; Nicodemus, U. S. 2,153,987.

[3] Dreyfus, U. S. 2,121,342; 2,176,958; Brit. 450,684; Fr. 808,712; Alexander Wacker Ges., Brit. 512,201; Fischer and Freytag, U. S. 2,339,066; 2,342,463.

[4] Barsky, U. S. 1,678,719; Bauer, Brit. 313,877; U. S. 1,829,208; Hurtley, Brit. 341,961; I. G. Farben., Brit. 259,204; Fr. 680,671; 689,275; Brit. 341,148;

XVII. ESTERIFICATION WITH ETHYLENE OXIDE

Ethylene oxide reacts with water to form glycol, with an alcohol to form a glycol ether, and with acetic acid to form glycol acetates:



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!O + CH_3COOH \rightarrow \underset{\text{Glycol Acetate}}{CH_3COOCH_2CH_2OH} \qquad (30)$$

$$CH_3COOH + CH_3COOCH_2CH_2OH \rightarrow \underset{\text{Glycol Diacetate}}{CH_3COOCH_2CH_2OCOCH_3}$$

The esterification reaction is carried out by passing the ethylene oxide into the heated acid containing sulfuric acid or a similar catalyst. Under these conditions, a second molecule of the acid, if available, will esterify the free alcohol group of the mono-ester to produce the diester of glycol.[1]

XVIII. ESTERS FROM ALDEHYDES

One molecule of an aldehyde reacts with another [reaction (31)] to give a molecule of ester:[2]

$$2RCHO \rightarrow RCOOCH_2R \qquad (31)$$

This reaction is thoroughly discussed by Child and Adkins.[3] The usual catalysts are aluminum and sodium alcoholates. Benzyl benzoate is manufactured in this way; furfuryl fuorate and other esters can be.[4]

The same may be accomplished by passing the vapor of the aldehyde over certain catalysts.[5]

When an aldehyde is boiled with acetanhydride, the acetate of the enol form is obtained:

$$RCH_2CHO + Ac_2O \rightarrow RCH{:}CHOCOCH_3 + CH_3COOH$$

This reaction has been known for some years but has not been exploited.[6]

Fr. 39,892; Matheson and Blaikie, Brit. 257,907; 264,143; Michael and Haag, U. S. 1,831,025; Pfeiffer, *Ber.*, **51,** 805 (1918); Pfeiffer, Engelhardt, and Alfuss, *Ann.*, **467,** 158 (1928); Schmidt and Niemann, Ger. 544,499; Spiegel and Szydlowsky, *Ber.*, **51,** 296 (1918).

[1] I. G. Farben., Brit. 265,233; 292,059; 302,041; Fr. 671,123; 685,433; Brit. 307,471; 332,267; Loehr, Can. 285,356; U. S. 1,701,424; 1,810,318; Monnet and Carter, Brit. 128,911; Steimmig and Ulrich, Can. 278,557; U. S. 1,817,425; Ger. 515,306; Fraenkel-Conrat and Olcott, *J. Am. Chem. Soc.*, **66,** 1420 (1944); Stein, U. S. 2,224,026.

[2] Tischenko, *J. Russ. Phys. Chem. Soc.*, **38,** 355 (1906).

[3] Child and Adkins, *J. Am. Chem. Soc.*, **45,** 3013 (1923); **47,** 798 (1925).

[4] Kamm and Kamm, "Organic Syntheses," Collective Vol. I, p. 102, John Wiley & Sons, Inc., New York, 1941; Nielsen, *J. Am. Chem. Soc.*, **66,** 1230 (1944); Kupinski and Nord, *Nature*, **151,** 363 (1943); Anselm and Kamler, Ger. 733,884; Bludworth, U. S. 2,250,520.

[5] Joshua *et al.*, U. S. 2,070,131; Abramova and Dolgov, *Chem. Abs.*, **34,** 4380 (1940).

[6] Schmidt, *Chem. Abs.*, **33,** 3331 (1939); Kaufler, U. S. 2,215,180.

XIX. ESTERS FROM ALCOHOLS

An ester may be prepared directly from an alcohol by passing it over a catalyst containing chromium at 375 to 425°C., usually under high pressure.

$$2C_2H_5OH \rightarrow CH_3COOC_2H_5 + 2H_2$$

This looks enticingly simple. For a time, there was considerable interest in it, but recently it has attracted little attention outside Russia.[1]

XX. ESTERS FROM CARBON MONOXIDE

Carbon monoxide, the anhydride of formic acid, unites with an alcohol at an elevated temperature and under high pressure, in the presence of a metal alcoholate, to give an alkyl formate:[2]

$$CH_3OH + CO \rightarrow HCOOCH_3$$

In the presence of acids or of boron fluoride and at somewhat higher temperatures, also under high pressure, the product is an acid:

$$CH_3OH + CO \rightarrow CH_3COOH$$

The acid so formed may react with a second molecule of the alcohol so that the final product is an ester.[3] A single molecule of an ether may react with carbon monoxide:[4]

$$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3$$

An olefin, an alcohol, and carbon monoxide may be made to unite. Processes involving carbon monoxide are of increasing importance.

XXI. ESTERIFICATION PRACTICE

DESIGN AND OPERATION OF ESTERIFICATION PLANT

BY THEODORE BAKER[6]

A plant for making esters from organic acids and alcohols on th large scale may be of three general types, depending on whether (1 the product is low boiling and is to be fractionated from an accumulate excess of water, as in the manufacture of methyl and ethyl acetates; (2) the ester is somewhat higher boiling and carries over with it considerable water that readily separates after condensation as a lower layer that can be decanted, as is the case with butyl and amyl acetates; or (3) the ester is of such low volatility that it is more practical to accumulate it in the still and merely volatilize the water and/or the excess of acid or alcohol if these cannot be made to react completely. Examples of this type are the ethyl and butyl phthalates.

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[1] Guinot, U. S. 2,136,613; Steik, U. S. 2,225,944; Scott, Can. 375,764; LEL'CHU and VELTISTOVA, *Chem. Abs.*, **32**, 2085 (1938); **35**, 2904 (1941); ABRAMOVA an DOLGOV, *Chem. Abs.*, **33**, 3759 (1939); KOTON, *Chem. Abs.*, **32**, 491 (1938): VASKEVIC and BULANOVA, *Chem. Abs.*, **33**, 3759 (1939); IVANNIKOV, *Chem. Abs.*, **34**, 7847 (1940

[2] Wietzel and Kremp, U. S. 1,698,573; Bartlett, U. S. 2,341,420.

[3] Dreyfus and Bader, U. S. 1,864,643; Du Pont, Fr. 808,040; Brit. 478,246; 534,69 536,422; Loder, U. S. 2,135,448; 2,135,451, 2,135,452; 2,135,453; 2,162,459: 2,211,62

[4] Dreyfus, U. S. 1,884,628; Woodhouse, U. S. 2,135,447; Loder, U. S. 2,135,44 McAlevy, U. S. 2,135,454; Larson, U. S. 2,135,450; Johnson, U. S. 2,273,269.

[5] Vail, U. S. 1,979,717; Can. 342,957.

[6] E. I. du Pont de Nemours & Company.

The first of these types of process may be run either as a batch or continuously. Both methods require efficient distilling columns, which may be of perforated plate or bell-cap design or even of the packed type. In every case, it is now customary to employ a catalyst, which is usually sulfuric acid, in admixture with the alcohol and acid that are to react. The function of this acid is not that of dehydration but merely to accelerate the reaction in the direction of equilibrium, and even less than 1 per cent is sufficient for the purpose. Esterification takes place to some extent even in the presence of large amounts of water and will continue as long as the acid and alcohol remain, if the ester is removed (by boiling) as fast as it is produced. In making ethyl acetate industrially, ethyl alcohol of 95 per cent by volume and acetic acid of 80 per cent or less concentration are generally used. There being no definite lower limit of acid concentration, it is merely a matter of economic balance as to how far the exhaustion of the acetic acid may be carried. About 1 per cent acetic acid to 99 per cent of water is not uncommonly attained with the use of a continuous process such as that of Backhaus, especially when using dilute acid to start with.[1]

Copper apparatus is generally used for large-scale esterification, as this metal is fairly resistant both to organic acids and to sulfuric acid when temperature and concentration are not excessive and free oxygen or compounds readily yielding oxygen are excluded. Steam coils, also of copper, are the usual means of heating. In the copper work, autogenous welding is to be preferred to brazing, although silver solder gives fair results. Gunmetal and phosphor bronze are to be preferred to brass, while chrome nickel steel (18–8) can be used on condensers but not in parts where sulfuric acid is used.

Class I. Low-boiling Esters: Fractionated from Accumulation of Water.—Figure I illustrates a batch still layout for making crude ethyl acetate and the like. The organic acid and alcohol are employed in about molecular proportions. At the start, the still can be filled to about four-fifths of its capacity. The catalyst H_2SO_4 may be added directly to the still charge or previously blended with the organic acid

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[1] Backhaus, U. S. 1,400,849; 1,400,850; 1,400,851; 1,400,852; 1,403,224; 1,403,225; 1,425,624; 1,425,625; 1,454,462; 1,454,463; Can. 211,675; 211,676; 217,703; 261,187.

The charge is brought up to the boil, and the whole distillate is refluxed for a time by closing the take-off valve *A*. The steam supply must be limited so that the condenser does not run hot or the pressure bottle show more than the normal back pressure of the column, this being about 1 to 1¼ in. per plate according to the design. After about an hour, the thermometer at the top of the column should read about 70°C. for ethyl acetate and remain steady, while the mid-column thermometer will gradually show a drop in temperature. When the latter indicates that several plates are charged with liquor boiling about 70°C., the take-off valve may be opened to bleed off the ethyl acetate as fast as it is formed and so hold the temperature in the mid-column practically constant. As the still charge diminishes owing to the formation and removal of ester, more acid and alcohol can be added gradually through the feed weir boxes to keep the still contents nearly constant in volume. The distillate is approximately the constant-boiling ternary mixture whose composition is 82.6 per cent ethyl acetate, 8.4 per cent ethyl alcohol, and 9 per cent water. Commonly, a slight excess of alcohol is present that prevents any separation into two layers, and a trace of

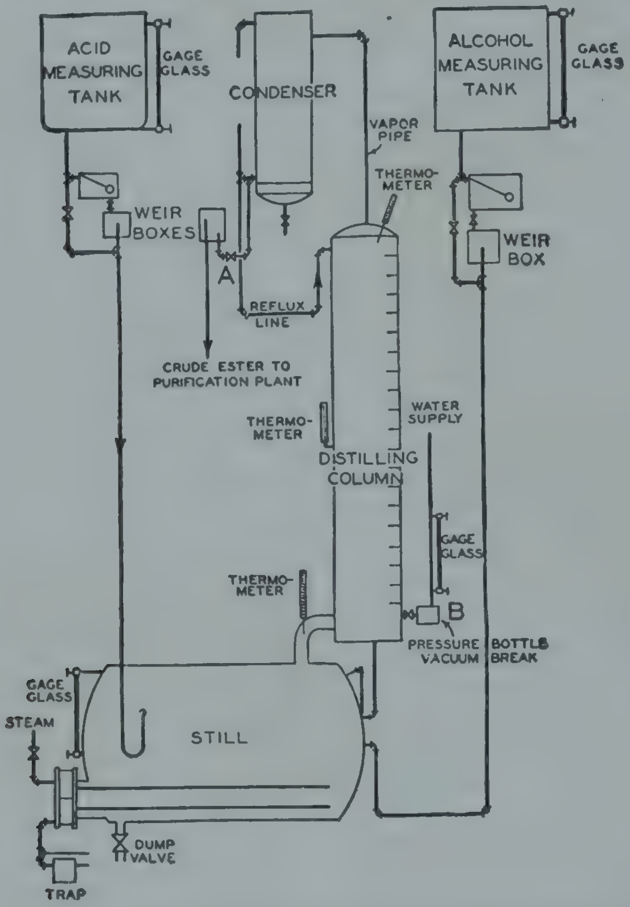
ACID MEASURING TANK
GAGE GLASS
CONDENSER
ALCOHOL MEASURING TANK
GAGE GLASS
VAPOR PIPE
THERMOMETER
WEIR BOXES
A
WEIR BOX
REFLUX LINE
CRUDE ESTER TO PURIFICATION PLANT
THERMOMETER
WATER SUPPLY
DISTILLING COLUMN
GAGE GLASS
THERMOMETER
B
PRESSURE BOTTLE
VACUUM BREAK
GAGE GLASS
STEAM
STILL
DUMP VALVE
TRAP

FIG. 1.—Layout: batch process for manufacturing ethyl acetate.

free acid is also present. This distillate is stored, to be purified in a separate apparatus later on. The exact boiling point of the ternary is reported as being 70.23, but, under manufacturing conditions, a variation of even 1° up or down is often noted due to the presence of small amounts of other materials.

As less water is carried over than is formed in the reaction

$$\begin{array}{ccccccc} \text{Acetic acid} & + & \text{alcohol} & = & \text{ester} & + & \text{water} \\ 60 & + & 46 & = & 88 & + & 18 \end{array}$$

and as the acid used will generally contain at least 20 parts of additional water and the alcohol about 4 parts, a fairly rapid accumulation of water is taking place in the still. This causes a slowing up of the reaction and requires a higher rate of reflux. After a while, the accumulation of water is so great that a cleanup is necessary. At this stage, an excess of alcohol is fed to the still, and the acid feed discontinued. The distillate is then diverted to another tank and reused in a following charge. When the acid and alcohol are sufficiently exhausted, the residual water is dumped, and the still recharged. The refining of the charge comprises neutralizing with sodium carbonate or lime under agitation, followed by water washing, which removes the excess of alcohol. The washing is often done countercurrent in a packed tube, the water flowing downward and the ester upward, the same apparatus acting as a decanter. The ester layer, holding about 4 per cent water in solution, has to be redistilled through a column. The distillate, which contains most of the water, is reseparated or rewashed, and the washings are separately redistilled to recover their contents of ester and alcohol, these being returned to the process. Formerly, calcium chloride was used to dry the ternary mixture, but this leaves a part of the alcohol unseparated, and a part of the calcium chloride stays in solution in the dried mixture. When such a mixture is redistilled, crusts are formed from which water is liberated at the end of the distillation.

A continuous process (Fig. 2) for making ethyl acetate, which is especially adapted to the utilization of dilute acetic acid, has been patented by Backhaus.[1] In this process, the residual acid water, exhausted of its acid and alcohol to as low a point as is economical, is promptly and continuously discharged from the apparatus. The regulation of the still is thus practically fixed. Another advantage is that the final purification and working up of the wash waters can be tied in with the production of the crude ester. Figure 2 illustrates the essentials of this process. The raw materials are first blended in the correct proportions and fed from the feed tank in a steady stream through a preheater into the esterifying column. From the top of this is taken off a mixture of about 20 per cent ester, 10 per cent water, and 70 per cent alcohol, while a suitable amount of the same distillate is refluxed back to the column at *A*. The ternary mixture taken off passes to the separating column at point *B*. Here it is rectified by closed steam in the calandria *C*. Part of the condensate is returned as reflux to the top of the column, and the take off goes to a proportional mixing device, where it is blended with about an equal volume of water, which causes a separation into two layers. These are settled out in the separator tank, the watery portion overflowing back to the lower part of the separating column, whence, blended with the alcohol and water accumulating in the base of this, it is passed by pipe *D* to a point in the esterifying column. On the lower plates of the column, the alcohol is exhausted and distills upward as vapor, while the slop water goes to waste at *E*. The washed ester, containing a little dissolved water and alcohol, overflows from the separator at *F* and enters the drying column in which a sufficient amount is distilled off to carry with it the water and alcohol, which may go either to the separating column or back to the mixer, washer, and separator. The dry ethyl acetate that accumulates in the calandria of the drying column is taken off through a cooler to the receiving tank *G*. In general, this ester, though dry and holding very little alcohol and free acid, needs to be redistilled before it can be placed on the market, because it may contain salts of copper and higher boiling esters formed from other acids present as impurities in the crude acetic acid employed.

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[1] Backhaus, *loc. cit.*

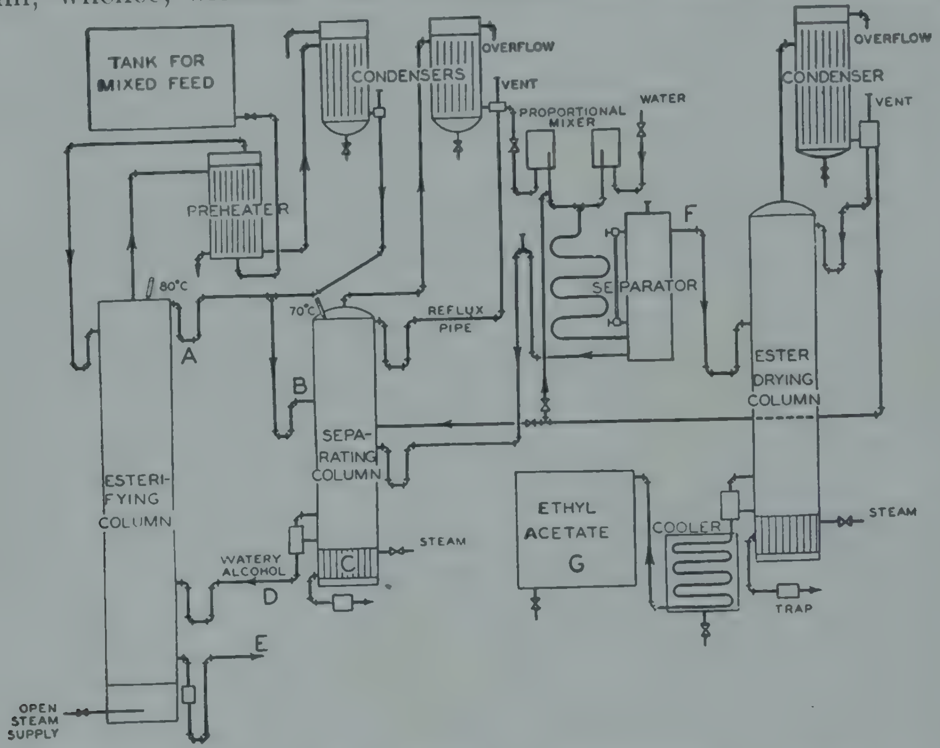
TANK FOR MIXED FEED
CONDENSERS
OVERFLOW
VENT
PROPORTIONAL MIXER
WATER
CONDENSER
OVERFLOW
VENT
PREHEATER
F
SEPARATOR
80°C
70°C
REFLUX PIPE
A
B
ESTER DRYING COLUMN
SEPA-RATING COLUMN
ESTERI-FYING COLUMN
ETHYL ACETATE G
COOLER
STEAM
STEAM
WATERY ALCOHOL
C
D
TRAP
E
OPEN STEAM SUPPLY

Fig. 2.—Layout: continuous process for manufacturing ethyl acetate.

The working up of crude ester made by the batch process is very similar to that employed in the continuous process, but, in the former, a special still must be provided for working up the weak wash waters unless this is done in the main batch still between esterification charges.

Class II. Esters Such as Butyl and Amyl Acetates.—This process differs from the first in that much more water is carried over with the ester when it distills from the esterification column or still. As this, in general, can exceed the total water formed during the reaction plus the free water in the raw materials, there is a general tendency for the still charge to go "dry." In any case, there is no building up of a watery still charge that has to be discharged as with ethyl and methyl acetates. Consequently, an apparatus (shown in Fig. 3) that is nearly as simple as that shown in Fig. 1 can be operated continuously over long periods. A separator is used from which part of the oil layer can be refluxed if necessary, while part of the reflux can be taken directly from the condenser without separation, depending on the amount of water to be eliminated. The distillate is always a ternary one, containing ester and alcohol as well as water. This is not, in general, objectionable, as a

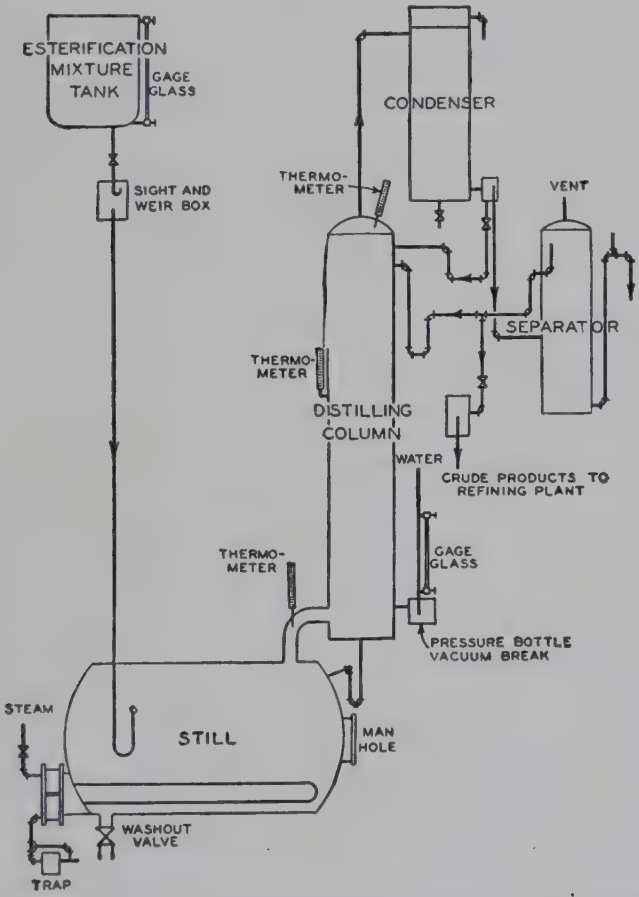
ESTERIFICATION MIXTURE TANK
GAGE GLASS
SIGHT AND WEIR BOX
CONDENSER
THERMOMETER
VENT
SEPARATOR
THERMOMETER
DISTILLING COLUMN
WATER
CRUDE PRODUCTS TO REFINING PLANT
THERMOMETER
GAGE GLASS
PRESSURE BOTTLE VACUUM BREAK
STEAM
STILL
MAN HOLE
WASHOUT VALVE
TRAP

FIG. 3.—Layout: for manufacturing butyl or amyl acetates.

product is often required that contains a certain proportion (10 to 15 per cent) of uncombined alcohol. The richness of the distillate in ester may be improved, if desired, by keeping the still charge stronger on the acid side. If an ester of 100 per cent is required, this may be obtained by rectification of the ester-alcohol mixture after drying. The foreshots in such a distillation contain a mixture richer in alcohol, whereas the tailings can be practically pure ester. The alcohol-rich fraction can be reworked in the esterfying process.

By employing an adequate reflux and avoiding too dry a column and still charge, the acetic acid can be substantially kept out of the distillate as it is carried down the column by the reflux, while the lower boiling ternary mixture accumulates in the heads. The lower temperature and the wetness of the charge also tend to check the formation of sulfur dioxide resulting from reduction of the sulfuric acid.

Class III. Esters of Very Low Volatility.—In this case, the ester does not appreciably volatilize with the water that forms or was originally present but stays behind in the still while the free acid and alcohol gradually diminish. In general, the arrangement shown in Fig. 3 may be used, merely changing the method of operation. In the case of ethyl alcohol derivatives, by adding benzene to the charge, the water can be eliminated by taking it off from the separator as a lower layer containing some alcohol, which can be rectified elsewhere and its alcohol recovered. In the case of butyl and amyl compounds, the use of benzene is unnecessary, as the employment of an excess of the alcohol serves the same purpose, the water going over as a binary with the alcohol and separating out in the same way. In the case of an easily volatilized acid, as acetic, the water may be eliminated as formed, by adding to the charge a compound such as dichloroethylene or ethyl acetate. Such substances form with water binaries of low boiling points; these concentrate at the top of the column and separate after condensation, the water layer being taken off, in one case at the top and in the other at the bottom.

When the reaction is practically complete, the sulfuric and excess of organic acid are neutralized, and the charge distilled to dryness, being finally heated in a high vacuum to eliminate low-boiling residues.

Other purification treatment, such as filtration, may be required finally to yield a first-class product.

PREPARATION OF BUTYL ACETATE. BATCH PROCESS[1]

It is important that the acetic acid used should be free from other acids; its water content is not so important. The butyl alcohol must be free from other alcohols and is used in about 10 per cent excess. The catalyst is about 0.1 per cent sulfuric acid.

[1] From information furnished by C. Barbre and O. B. Helferich.

The still (Fig. 3) is heated under total reflux until the temperature at the top of the distilling column becomes constant at approximately 89°C. Then the distillate is withdrawn from the condenser as rapidly as can be done without permitting the temperature to rise above 90°C. (89.4°C. being the boiling point of the ternary of ester, alcohol, and water). The percentage composition of the distillate after separation into two layers is given in Table VI.

TABLE VI

Layer	%	Ester, %	Butyl alcohol, %	Water, %
Upper.......	75	80.5	13.4	6.1
Lower............	25	1.92	1.69	97.39

These layers are separated continuously in an automatic separator; the upper layer is returned to the still, while the lower is taken off and measured. As the reaction nears completion, the amount of water that separates diminishes until there is none; the temperature in the still, after rising steadily, flattens out at the refluxing temperature of the butyl acetate. The crude ester is cooled and neutralized with aqueous sodium hydroxide. After separation of the water layer, the ester is ready for refining by distillation. The first fraction is the ester-water binary which is caught in an automatic separator, from which the ester layer is returned to the still. The next is a small fraction that contains some water, as shown by turbidity when it is mixed with 10 volumes of benzene. This is added to the next batch. The rest of the distillate is finished ester and goes to storage.

A kettle of 2,000-gal. capacity with a 30-plate, 30-in. column can produce 1,000 gal. of finished ester in 48 hr., provided that anhydrous acetic acid and butanol are used. The presence of any considerable amount of water decreases the capacity of the apparatus and lengthens he distillation time.

PREPARATION OF DIBUTYL PHTHALATE

The raw materials used in industry for preparation of dibutyl phthalate are the commercial grades of phthalic anhydride and butyl alcohol; he latter may be saturated with water (20.1 per cent at 20°C.). The atalyst is 0.1 per cent sulfuric acid, based on the total charge to the kettle.

The equipment used for the reaction is substantially as shown in Fig. , except that the kettle is equipped with a hopper and screw conveyor for charging the phthalic anhydride, in the form of a granular solid, and a circulating pump. The reaction kettle should preferably be made of stainless steel. The butyl alcohol is charged in 30 per cent molar excess. This excess serves the two purposes of securing practically complete reaction of the anhydride and of dehydrating the ester as the reaction proceeds, by removal of the water from the separator as the lower layer of the heterogeneous binary distillate (b.p., 93.0°C. at 760 mm. Hg).

The composition of the two layers of the distillate is given in Table VII.

TABLE VII

Layer	% Ester	% Butanol	% Water
Upper	55.5	77.5	22.5
Lower	44.5	8.0	92.0

The reaction is complete when water ceases to come over with the distillate or a sample from the kettle contents shows a constant, low acidity.

The excess butanol is then removed from the kettle by distillation with no reflux. The residual acidity, consisting mostly of the sulfuric acid catalyst with a small amount of organic acids, is neutralized with a lime-water slurry containing 200 per cent excess lime over the calculated equivalent. The mixture in the kettle is agitated by the circulating pump until the pH of the ester layer is practically 7.0, when the water is stripped from the kettle under high vacuum, the last traces being removed by sparging with an inert gas.

The residual product can be filtered to give an acceptable grade of ester for many purposes. In order to produce a first-class product, distillation of the ester under high vacuum is usual.

ESTER GUM

BY EINAR WEST[1]

The equipment is an autoclave with a reflux condenser, kept warm enough to let water vapor pass but cool enough to return the glycerol. Molten rosin and 10 to 12 per cent of its weight of glycerol are run in and heated at such a rate that the foaming is not excessive. The course of the reaction is followed by removing samples and determining the acid number. When this falls below 20, the product is discharged into a cooling pan or directly into metal containers. The autoclave may be subjected to vacuum before discharge to rid it of any low-boiling substances that may have been present in the rosin or produced by decomposition.

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[1] Hercules Powder Company.

TERPENE ESTERS BY DIRECT ADDITION OF ALIPHATIC ACIDS

BY J. N. BORGLIN[1]

Terpene esters can be made by the direct addition of fatty acids,[2] halogenated[3] and thiocyanated[4] fatty acids to terpene hydrocarbons, ethers, and esters. Since the bicyclic terpenes (camphene, α-pinene, and β-pinene) are more reactive than the monocyclic, they are the preferable starting materials.

Whether the ester formed is predominately secondary or tertiary depends upon the terpene used. In the case of camphene, the addition is preceded by isomerization, and the ester is secondary. The pinenes give a mixture in which the tertiary esters predominate, the ratio of tertiary to secondary depending on the reaction conditions.

The addition is carried out at a fairly low temperature, preferably below 100°C., in order that the tendency to isomerize to monocyclic terpenes and to polymerize may be minimized. On account of the corrosive nature of the fatty acids used, glass-lined equipment is required.

As a typical example: A mixture of 1,100 parts by weight of turpentine and 750 parts of monochloracetic acid is kept at 50 to 55°C. for 8 hr. under a blanket of carbon dioxide. The product is washed with cold water to remove unreacted acid and distilled with steam to recover the uncombined terpene. The yield of isomeric esters is about 60 per cent. The product is light in color; a water-white ester can be obtained by flash distillation in vacuum.

ACETYLATION OF CELLULOSE

In the space available here, it is possible to do no more than present a brief outline of the general technical features of the production of cellulose acetate. A list of books and references to several recent reviews and patents are given below.[5,6,7]

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[1] Hercules Powder Company.

[2] BOUCHARDAT and LAFONT, *Compt. rend.*, **102,** 171 (1886).

[3] Borglin, U. S. 2,217,611; 2,217,613; 2,217,614; 2,227,059; 2,227,060; 2,239,495; 2,275,606.

[4] Borglin, U. S. 2,227,061

[5] WORDEN, "Technology of Cellulose Esters," Vol. VIII (1916); "Technology of Cellulose Ethers," Vol. II, 1933; Reinhold Publishing Corporation, New York, LIPSCOMB, "Cellulose Acetate," 1933; MULLIN, "Acetate Silk and Its Dyes," 1927, KRÜGER, "Zelluloseazetate und die andern organischen Ester der Zellulose," Steinkopff, Dresden, 1933.

[6] YARSLEY, "British Plastics Yearbook," 49–55 (1932) (a short review); CHAUMETON and YARSLEY, "British Plastics," 1929–1931 (an extended series of articles); Review of Patents," *Brit. Plastics*, **13,** 352, 424, 487 (1942); **14,** 41, 105, 163, 218. 284 (1943).

[7] Malm and Hiatt, U. S. 2,172,250; Dreyfus, U. S. 2,261,237; Seymour and White, U. S. 2,264,411, 2,285,536; Hofmann and Simson, U. S. 2,315,203; Hofmann and

The product of the acetylation of cellulose is the triacetate (containing 44.8 per cent of acetyl), which may be represented by the empirical formula $C_6H_7O_5(CH_3CO)_3$. The reaction by which this product is formed is not so simple as, for example, the esterification of ethyl alcohol. Attempts to acetylate cellulose with glacial acetic acid alone, even in the presence of dehydrating agents or catalyst, have not been successful; a more effective acetylating agent is required, such as acetyl chloride or acetic anhydride. With the latter reagents, the reaction for the formation of a single triacetate unit may be represented as follows:

$$C_6H_{10}O_5 + 3CH_3CO{\cdot}Cl \rightarrow C_6H_7O_5(CH_3CO)_3 + 3HCl \qquad (a)$$

$$C_6H_{10}O_5 + 3(CH_3CO)_2O \rightarrow C_6H_7O_5(CH_3CO)_3 + 3CH_3CO{\cdot}OH \qquad (b)$$

best results being obtained when a catalyst is present. The cellulose (usually bleached cotton linters) may be caused to react with the vapors of foregoing reagents or in the presence of a liquid medium that does not dissolve the cellulose acetate formed, such as benzene or carbon tetrachloride, or the reaction may be caused to take place in the presence of acetic acid, liquid SO_2, or other solvents for the cellulose acetate.

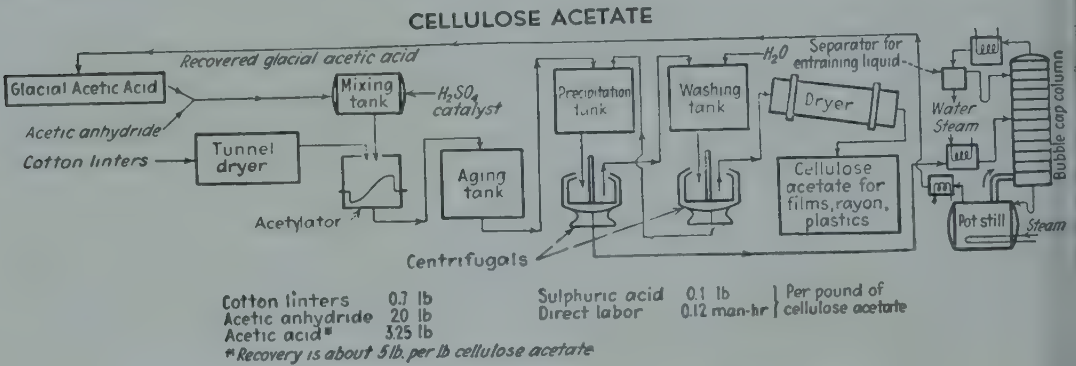
CELLULOSE ACETATE
Recovered glacial acetic acid
Glacial Acetic Acid
Acetic anhydride
Cotton linters
Mixing tank
H₂SO₄ catalyst
Tunnel dryer
Acetylator
Aging tank
Precipitation tank
Washing tank
H₂O
Separator for entraining liquid
Dryer
Cellulose acetate for films, rayon, plastics
Water
Steam
Bubble cap column
Pot still
Steam
Centrifugals
Cotton linters 0.7 lb
Acetic anhydride 2.0 lb
Acetic acid* 3.25 lb
Sulphuric acid 0.1 lb
Direct labor 0.12 man-hr
Per pound of cellulose acetate
*Recovery is about 5 lb. per lb cellulose acetate

FIG. 4.—Flow sheet: cellulose acetate manufacture.

Cellulose triacetate itself has been of little industrial importance, chiefly because of its limited solubility in the common nontoxic solvents; it is receiving increased attention as new solvents are developed. Since, however, cellulose as usually acetylated yields a triacetate only, it is necessary to prepare it as an intermediate product in the production of commercially useful solvent-soluble acetates. These more soluble secondary acetates are formed by partial hydrolysis of the primary acetate.

In spite of the numerous alternative methods cited for the preparation of cellulose acetate, one procedure is most commonly used; in this method, the cellulose reacts with acetic anhydride in the presence of glacial acetic

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Röhm, U. S. 2,317,767; Malm and Blanchard, U. S. 2,353,255; Marschall, Ger. 710,851; Koetschet, Ger. 710,307.

acid and a catalyst, usually sulfuric acid. A large number of other catalysts have been proposed, among them being zinc chloride, perchlorates, mixtures of sulfuric and phosphoric acid, acid sulfates, phosphorus and sulfur chloride, and sulfonic acids.

Although the acetylation of cellulose by acetic anhydride may be represented chemically by the simple equation (*b*) shown above, the reaction is greatly complicated by the physical and colloidal characteristics of the cellulose and of the cellulose acetate formed. The esterification reaction proper is accompanied by (1) degradation of the cellulose and (2) dispersion of the resulting cellulose acetate in the glacial acetic acid present. The heterogeneous nature of the reaction mass and the high viscosity of the resulting product require special means of agitation in order to secure uniformity of results. The equipment for this purpose, which must, of course, be resistant to corrosion by the reagents, sometimes takes the form of a rotating vessel of the ball-mill type, with or without baffles and of varied shapes, and in other cases is a heavily constructed agitated vessel of the dough-mixer type.

Close attention must be given to the time and the temperature of the reaction and the amount of catalyst used. As a further insurance of uniformity of reaction, the cellulose is usually subjected to a pretreatment prior to the acetylation; a rather large number of pretreatments have been suggested, their principal purpose being to get the cellulose into such a physical form that it will be uniformly reacted upon. Among the materials suggested are formic acid, acetic acid, alkalies, oxidizing agents, sulfuric acid, lactic acid, etc.

The primary stage of acetylation is complete when the cellulose has finally dissolved owing to the formation of the soluble cellulose triacetate. When this point is reached, as determined by the complete disappearance of the cellulose fibers, either the resulting clear viscous solution may be diluted with sufficient water or other diluent to precipitate the triacetate, or the latter may first be converted into the secondary acetone-soluble acetates, which contain between 41 and 37 per cent of acetyl.

This conversion is caused to take place by introducing into the mass sufficient water to effect the desired hydrolysis within a convenient time. The amount of water added, the amount of hydrolysis catalyst (usually sulfuric, phosphoric, or hydrochloric acid), and the time and temperature of the hydrolysis differ widely in practice. In some cases, this *ripening* is allowed to take place at room temperature over a period of several days, whereas in others, at an elevated temperature (40 to 60°C.), it may take place in a few hours. The progress of the reaction may be followed by periodically removing samples of the solution, precipitating the cellulose acetate, and determining its composition (percentage acetyl) or observing its solubility in different solvents.

When the reaction has proceeded to a point where a product of the desired composition is obtained, the cellulose acetate is precipitated from the solution. Numerous methods of precipitation have been described.[1] The more common one consists in flowing the viscous acetic acid solution into an excess of water, with suitable agitation, in such proportions that the resulting supernatant liquor is below the concentration in acetic acid which will soften the cellulose acetate. This supernatant acetic acid may be drawn off and recovered; the precipitated acetate is then washed with water until it is acid free, after which it may be dried under controlled conditions in any one of the usual technical driers.

The product of primary acetylation, upon analysis, usually shows about 44.0 per cent of acetyl instead of the theoretical 44.8 per cent; the remaining hydroxyl groups appear to have been esterfied by sulfuric acid. A product of this composition is distinctly unstable toward heat and toward hydrolysis, and the combined sulfuric acid must be removed in order to obtain a stable material. This removal is effected during the ordinary hydrolysis to the secondary acetate, although in some cases additional means of stabilizing the precipitated acetate are considered necessary.

The cellulose acetate thus prepared is a white, fibrous or flaky material, of specific gravity 1.3, having ready solubility in acetone, from which it can be deposited as a tough, transparent, flexible film upon evaporation of the solvent. The cellulose acetates of commerce are characterized by two important properties:

1. Viscosity, usually measured in acetone solution.
2. Composition, as percentage of acetyl.

The range of possible viscosities is rather wide, thus permitting the adaptation of the product to various uses. The usual range of acetyl values is between 37 and 41 per cent, solubility in different solvents being greatly dependent upon the precise composition.

In addition to the above variable properties representing the type of the cellulose acetate are certain others that indicate its stability, uniformity, and general quality. An acetate is usually examined with respect to its moisture content (which may be as high as 6 per cent, depending upon relative humidity conditions), the free acid present, the stability toward heat or toward hydrolysis, and the completeness of its solubility in the solvent (usually acetone) in which it is to be used.

THE XANTHATION OF CELLULOSE

BY W. D. NICOLL[2]

The xanthation of cellulose and the spinning of the viscose are represented in the flow sheet (Fig. 5). The cellulose, which may be bleached wood pulp or cotton linters or a mixture of the two, in sheets, is placed in a steeping tank, which is also a press. It is impregnated with a caustic soda solution of definite strength—usually 17.5 to 18 per cent—and then pressed out until the wet weight bears the desired relation to the dry. This material, called *alkali cellulose*, is shredded in Werner and Pfleiderer shredders having serrated edges and saddle. The shredded alkali cellulose, which in physical appearance resembles moist bread crumbs, is loaded into boxes which are stored in a constant-temperature room for a definite time to effect the *aging*. During this period, the oxygen of the air acts on the cellulose and brings about a reduction of the viscosity of solutions made from it. In the next step, which is carried out at constant temperature in a rotating drum called a baratte, the alkali cellulose is treated with a definite amount of carbon disulfide in vapor form. At the completion of the reaction, the orange-yellow cellulose xanthate is agitated with a definite amount of caustic soda solution. The resultant solution, or dispersion, is the viscose. This, in turn, must be aged, or ripened, to a state that has been shown by experience to give the best results in spinning. If the viscose is ripened too long, it sets to a gel, which cannot be spun or sheeted. The ripened viscose is deaerated and filtered before

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[1] U. S. 1,899,061; 1,844,017.

[2] E. I. du Pont de Nemours & Company.

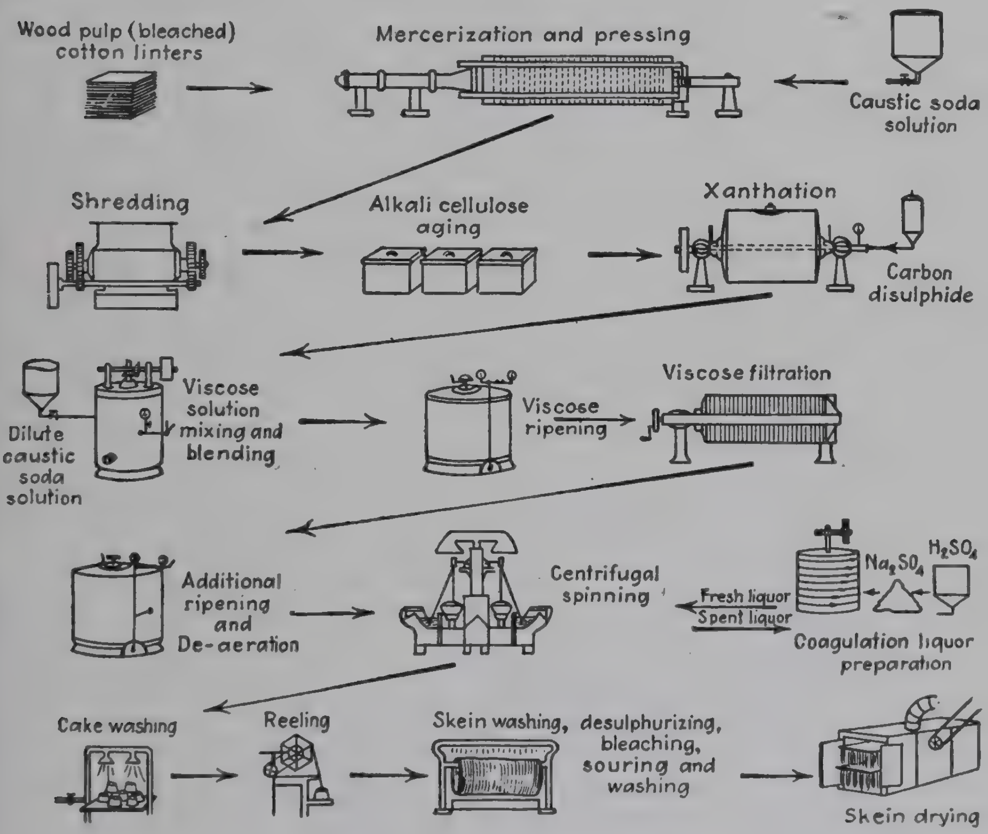
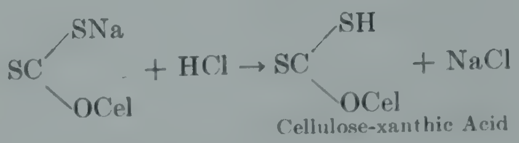

Wood pulp (bleached) cotton linters
Mercerization and pressing
Caustic soda solution
Shredding
Alkali cellulose aging
Xanthation
Carbon disulphide
Dilute caustic soda solution
Viscose solution mixing and blending
Viscose ripening
Viscose filtration
Additional ripening and De-aeration
Centrifugal spinning
Fresh liquor
Spent liquor
Na_2SO_4
H_2SO_4
Coagulation liquor preparation
Cake washing
Reeling
Skein washing, desulphurizing, bleaching, souring and washing
Skein drying

FIG. 5.—Cellulose xanthate.

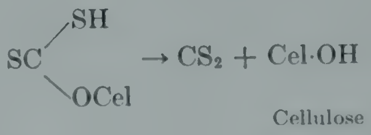
being forced through small holes into a salt-acid bath in the spinning of rayon or through a slot for making Cellophane.

When sodium cellulose-xanthate is brought into contact with acid, cellulose-xanthic acid is set free:



$$SC\begin{matrix}\nearrow SNa\\ \searrow OCel\end{matrix} + HCl \rightarrow \underset{\text{Cellulose-xanthic Acid}}{SC\begin{matrix}\nearrow SH\\ \searrow OCel\end{matrix}} + NaCl$$

The free cellulose-xanthic acid is unstable and decomposes into carbon disulfide and cellulose:



$$SC\begin{matrix}\nearrow SH\\ \searrow OCel\end{matrix} \rightarrow CS_2 + \underset{\text{Cellulose}}{Cel{\cdot}OH}$$

The regenerated cellulose is in the form of fine threads or sheets

MANUFACTURE OF GLYCERYL TRINITRATE (NITROGLYCERIN)

BY J. L. BENNETT[1]

Glycerol [$C_3H_5(OH)_3$], a by-product of soap manufacture, is a sweet, sirupy liquid at ordinary temperatures but freezes when exposed for a long time at temperatures below 10°C. (50°F.), especially if crystals of frozen glycerol are introduced into the material. Glycerol produced for the manufacture of glyceryl trinitrate [nitroglycerin, $C_3H_5(O{\cdot}NO_2)_3$] generally contains not less than 98.72 per cent glycerol (sp. gr., 1.2620 at 15.6°C./15.6°C.).

Since the freezing point of glyceryl trinitrate is about 13.3°C. (56°F.) and many commercial explosives are required for use in cold weather, the freezing point of nitroglycerin is lowered by adding varying percentages of ethylene glycol [$C_2H_4(OH)_2$] to the glycerol before nitration or by polymerizing part of the glycerol to diglycerol [$C_6H_{10}O(OH)_4$]. Commercial ethylene glycol for nitration should contain not less than 99 per cent ethylene glycol. The specific gravity should be 1.116 to 1.119 at 15.6°C./15.6°C. Ordinary cane sugar (sucrose, $C_{12}H_{22}O_{11}$) also may be dissolved in dynamite glycerol, either with or without ethylene glycol or diglycerol, and satisfactorily nitrated.

Therefore, the nitrated product prepared for use in commercial explosives may be glyceryl trinitrate or a mixture of this ester with varying percentages of either one or more of the following products:

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[1] Hercules Powder Company.

Ethylene dinitrate	$C_2H_4(O\cdot NO_2)_2$
Diglyceryl tetranitrate	$C_6H_{10}O(O\cdot NO_2)_4$
Sucrose octanitrate	$C_{12}H_{14}O_3(O\cdot NO_2)_8$

The process of making nitroglycerin, either with or without the other esters, comprises four principal steps, *viz.*, nitration proper, separation, prewashing, and neutralization. The process consists of adding glycerol slowly to a suitable charge of mixed nitric and sulfuric acids to form nitroglycerin and spent acid; separating nitroglycerin from spent acid; washing the nitroglycerin with water to remove most of the dissolved or entrained acids; and neutralization of the remaining acids with an alkali to give a neutral and stable nitroglycerin.

Equipment.—The *nitrator* is a covered cylindrical steel vessel provided with mechanical agitators. Steel coils are located around the inside wall of the nitrator so that heat liberated by the reaction may be removed by circulating brine through them. The bottom of the nitrator slopes to an iron- or chemical-ware cock, which allows the mixture of spent acid and nitroglycerin to be discharged to the separator. The nitrator is equipped with indicating thermometers for control of the temperature of nitration. Situated at one side and above the nitrator is a small scale-tank holding the glycerol for one charge.

The *separator* is a shallow lead vessel with open top, located close to the nitrator but on a lower level. The bottom slopes to an outlet cock of chemical ware, and thermometers are provided at two levels to indicate the temperature of the spent acid and nitroglycerin. A rectangular plate-glass window is cemented in the side of the separator to permit inspection of the mixture. A large tank containing water is installed below the nitrator and separator so that their contents can be discharged into it if the operation does not proceed normally.

The outlet from the separator discharges spent acid into a pipe line leading to the spent-acid storage and discharges the nitroglycerin to the *prewash tank.* This is a partially covered wooden or lead tank provided with a vent pipe in the cover and an outlet at the bottom. Through the bottom outlet, the nitroglycerin is delivered to the *neutralizing tank*, which is a vertical, cylindrical, lead tank provided with a cover and vent pipe and bottom outlet. The prewash and neutralizing tanks are equipped with air agitators for mixing the nitroglycerin and wash waters. The agitators are usually made of hard rubber in the form of a hub and hollow spokes, the spokes being drilled with small holes to distribute the air uniformly up through the contents of the tank.

Small, open-top labyrinths (baffled boxes) are provided at suitable points, so that all wash waters can pass through them in order to settle out any suspended nitroglycerin. The effluent may then be discharged safely into the drainage system.

Operation.—The acid mixture usually consists of approximately equal parts of nitric and sulfuric acid and has a total acidity of close to 100 per cent. The composition of the mixture varies with the total acidity, and the relative percentages of nitric and sulfuric acid are adjusted so that with the water liberated during nitration, the composition of the spent acid is approximately the same in all cases. The mixed acid should be well settled before use so as to contain a minimum of suspended impurities, such as iron sulfate, which will interfere later with the separation of nitroglycerin from the spent acid.

A definite weight of mixed acid is placed in the nitrator, and a definite amount of glycerol, calculated from the nitric content of the mixed acid being used, is delivered into the glycerol scale tank. The mechanical agitator is started, and brine circulated through the coils until the acid mixture is reduced to the desired nitrating temperature. Although a predetermined temperature is maintained during nitration, this temperature may vary from 2.2°C. (36°F.) to 7.7°C. (46°F.) or higher, at different plants.

When the thermometer registers the desired temperature, the glycerol is allowed to run continuously into a nitrator at a rate that maintains the temperature at the desired point. The reaction is very rapid, so that within 3 to 5 min. after the last of the glycerol is in the nitrator, the mixture is discharged to the separator. In order to facilitate separation of the nitroglycerin from the spent acid, a small amount of material such as sodium fluoride is added to the nitrator charge prior to delivery to the separator.

The charge of mixed acid used in the United States is approximately 7,000 lb. The glycerol used with it is approximately 1,500 lb. and produces about 3,500 lb. of nitroglycerin. The time required for nitration depends on the capacity of the brine system to remove the heat of reaction and, in general practice, varies from 60 to 90 min. per charge.

The spent acid-nitroglycerin mixture discharged from the nitrator is allowed to remain quietly in the separator from 45 to 60 min., during which time the nitroglycerin, having a specific gravity of 1.6, gradually separates from and rises to the surface of the acid. The progress of the separation is observed through the plate-glass window in the side of the separator. A distinct line of demarcation between the nitroglycerin and spent acid indicates when the separation is satisfactorily completed.

The spent acid is delivered through the bottom outlet cock and pipe line to the spent-acid storage tanks, and the nitroglycerin, carrying dissolved and entrained nitric and sulfuric acids, is delivered to the prewash tank, which is partly filled with warm water. By means of air agitation, the nitroglycerin is intimately mixed with the wash water, which dissolves the greater portion of the acid. The nitroglycerin is allowed to settle from the acid water and is then delivered to the neutralizing tank, which is generally located in another building. Delivery is made through a covered wood gutter, lined with sheet rubber.

The nitroglycerin enters the neutralizing tank, which contains a warm, dilute water solution of sodium carbonate, and the gutter is flushed down with an additional quantity of sodium carbonate solution to wash all the nitroglycerin into the neutralizing tank.

The nitroglycerin and alkaline water are intimately mixed by air agitation until a sample of the nitroglycerin is neutral. Litmus paper is sometimes used to test for neutrality, but the pH method is more reliable. The neutral nitroglycerin is very stable and, after being settled from the wash water, is ready for use in commercial explosives.

All waste waters from the preliminary washing and sodium carbonate neutralizing operation, as well as the water used for washing out equipment used in the process, are passed through settling tanks in which small amounts of suspended nitroglycerin are settled out and returned to the washing tanks.

The spent acid delivered from the separator to storage tanks is passed through a recovery operation. The nitric acid and nitrogen oxides are separated from the sulfuric acid by denitration with the aid of steam in a suitable tower (see chapter on Nitration). Typical spent acids from the nitration of glycerol will analyze 74 to 75 per cent H_2SO_4 and 8 and 9 per cent HNO_3 when the total nitrogen present is calculated to HNO_3. The spent acid contains nitroglycerin in solution, which is safely decomposed by the heat evolved by the interaction of steam and the acid mixture.

Simple calculations will show that 100 lb. of pure glycerol should produce 246.61 lb. of glyceryl trinitrate and would require 205.31 lb. of nitric acid. Likewise, 100 lb. of pure ethylene glycol should produce 245.03 lb. of ethylene dinitrate with a consumption of 203.09 lb. of nitric acid. In practice, an excess of 10 to 15 per cent of nitric acid is provided in the mixed acid and is recovered from the spent acid.

In average practice in the United States, the yield of nitroglycerin is 96 to 97 per cent of the theoretical amount, while approximately 3 per cent is lost by solution in the spent acid. Small amounts are also lost by solution in the wash waters (see Chapter I).

The manufacture of glyceryl trinitrate and similar esters may be classed as an extremely hazardous operation unless conducted under suitable conditions and in properly designed equipment. It should never be undertaken, even on a small scale, by anyone who is not fully informed and not protected by approved safety devices.

THE MANUFACTURE OF CELLULOSE NITRATE

(Commonly called Nitrocellulose)

BY E. E. THOENGES[1]

When cellulose $(C_6H_{10}O_5)x$ is treated with mixed acid, it undergoes nitration readily, and the reaction for the highest nitrate may be presented as follows:

$$C_6H_7O_2(OH)_3 + 3HONO_2 \rightarrow C_6H_7O_2(O\cdot NO_2)_3 + 3H_2O \qquad (N = 14.16\%)$$

The nitrogen content of any particular nitrate largely defines its solubility and other properties and, consequently, its technical application. The relationship between the nitrogen content and industrial application is as follows:

% Nitrogen	
10.7–11.2	Chiefly used in plastics with camphor as plasticizer. Completely soluble in ethanol-toluene mixtures. Low percentages largely soluble in ethanol
11.2–11.7	Used in lacquer containing considerable ethanol. Soluble in methanol, ether-alcohol, ester-hydrocarbon mixtures, etc.
11.8–12.2	Most common range for lacquers, artificial leather, and films. Soluble in esters, *e.g.*, ethyl, butyl, and amyl acetates. Ester solvents will tolerate considerable hydrocarbon. Also soluble in ether-alcohol and acetone
2.5–13.5	Chiefly used in smokeless powder. Soluble in acetone or esters

Two forms of cellulose are generally employed for nitration, *viz.*, purified cotton linters and the better grades of bleached sulfite pulp. Cotton linters have previously been the chief raw material, but, within recent years, methods have been developed for the preparation of wood pulp for industrial nitrations, and this source of cellulose is used very extensively at present.

The three major steps of the process are nitration, purification, and dehydration.

Nitration.—Forty pounds of dried and loosely formed cellulose is forked into the nitrating dipping pots and thoroughly agitated in a large excess of mixed acid for 20 to 30 min. at a temperature of 20 to 40°C. The mixed acid varies widely for the different types of nitrocellulose but may have an approximate composition of 25 per cent nitric acid, 55 per cent sulfuric acid, and 20 per cent water, which gives a product containing approximately 11.5 per cent nitrogen.

After nitration, the charge is dropped into centrifugals to remove the spent acid. The acid-wet nitrocellulose is quickly forked from the sides of the basket of the centrifugal and dropped into water in immersion bowls. The nitrocellulose is then floated in a stream of water to the purification area. The spent acid is analyzed and fortified with strong nitric and sulfuric acids to the proper composition for reuse.

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[1] Hercules Powder Company.

Purification.—The first step in the purification process is the removal of the retained acid from the nitrocellulose by washing. The nitrocellulose suspended in water is then pumped by a centrifugal pump to the boiling tubs where it is heated by injection of live steam. This operation breaks down unstable cellulose compounds, formed during nitration, into a condition whereby they may be washed out. "Straight" nitration types are then pumped to treating tubs, given additional washes or treatment, depending upon their ultimate use, and blended for viscosity. Low-viscosity types are spoken of as *digester types* and are pumped from the boiling tubs to the digester building.

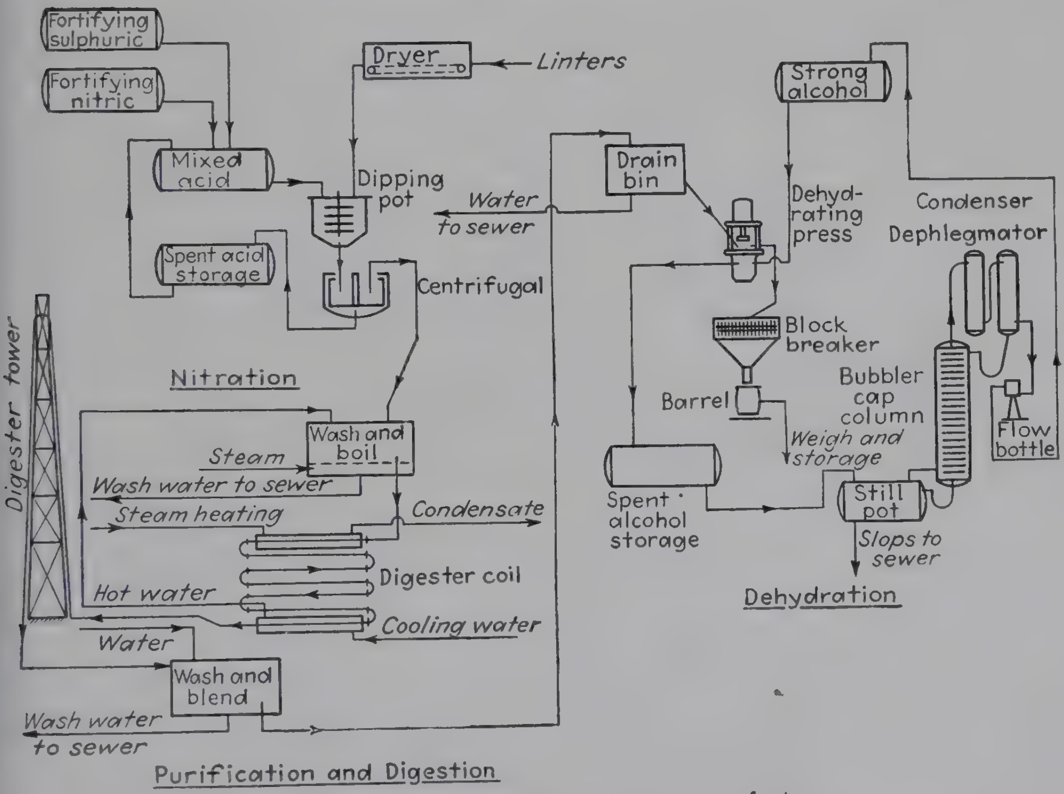
Fortifying sulphuric
Fortifying nitric
Dryer
Linters
Strong alcohol
Mixed acid
Dipping pot
Water to sewer
Drain bin
Dehydrating press
Condenser
Dephlegmator
Spent acid storage
Centrifugal
Digester tower
Block breaker
Nitration
Bubbler cap column
Barrel
Flow bottle
Wash and boil
Steam
Weigh and storage
Wash water to sewer
Steam heating
Condensate
Spent alcohol storage
Still pot
Slops to sewer
Digester coil
Hot water
Dehydration
Cooling water
Water
Wash and blend
Wash water to sewer
Purification and Digestion

FIG. 6.—Flow sheet: cellulose nitrate manufacture.

Reduction in viscosity may be effected by chemical treatment with ammonia, but pressure digestion is generally used and is a more satisfactory process. Pressure digestion was formerly carried out in large pressure vessels, and this process is still used to some extent in Europe. In the United States, however, pressure digestion is accomplished in a Milliken continuous digester. This equipment consists of a 4-in. jacketed coil approximately 4,000 ft. long made entirely of chrome steel. At the discharge end of the digester, the pipe line rises over a 200-ft. tower and thereby provides a hydrostatic back pressure. Pumping against the hydrostatic leg and friction in the system result in a pressure of 100 lb. per sq. in. inside the coil. It is possible, therefore, to heat a nitrocellulose-water mixture to a temperature of about 160°C. During a 20-min. passage through the digester, the viscosity of the nitrocellulose is substantially and uniformly reduced. The mixture is cooled by water jackets before it flows over the digester tower. Like the straight nitration types, the digester types are then pumped to treating tubs.

Dehydration.—Following purification, the product is pumped to chrome-steel drain bins. After the excess water has drained off, the wet nitrocellulose is dehydrated. About 60 lb. of the water-wet product are placed in a hydraulic press, and 250 lb. pressure applied for a short time. The dehydrating agent, usually denatured ethyl alcohol, is then pumped through the block in the press to displace the remaining water. The pressure in the press is then increased to 3,000 lb., reducing the excess alcohol to something less than 30 per cent of the weight of nitrocellulose. The blocks so formed are then put through a breaker and dropped into barrels for shipment. The weak alcohol produced in dehydration is rectified in standard alcohol stills for reuse.

CHAPTER XI

HYDROLYSIS

BY STEWART J. LLOYD AND G. D. PALMER, JR.

I. DEFINITION AND SCOPE

The term *hydrolysis* is applied to reactions of both organic and inorganic chemistry wherein water effects a double decomposition with another compound, hydrogen going to one component, hydroxyl to the other:

$$XY + H_2O \rightarrow HY + XOH$$
$$KCN + H_2O \rightarrow HCN + KOH$$
$$C_5H_{11}Cl + H_2O \rightarrow HCl + C_5H_{11}OH$$

For inorganic chemistry, hydrolysis is usually the reverse of neutralization, but in organic chemistry its scope is broader. Here it includes, among other things, the inversion of sugars, the breaking down of proteins, the saponification of fats and other esters, and the final step in the Grignard reaction, all of which can be carried on with water alone, albeit slowly and incompletely. For convenience, the meaning of the term has been extended to cover also the numerous cases in which an alkali is added to the water and in which the alkali salt of an acid is usually one of the final products:

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Even more common is the application of the term to reactions in which an acid is added to the water in large or small amounts. This addition, like that of alkali, invariably hastens the hydrolysis even if it does not initiate it. The saccharification of cellulose, wherein glucose is produced as an intermediate product in the making of alcohol from wood, and the enormous production of glucose from starch fall in this category. Accelerating agents other than acid and alkali are known but, with the single exception of enzymes, are not important. The enzymes (organic catalysts) are of surpassing importance in vital processes, both animal and plant, especially in preparing food for use in the body, and many of the reactions catalyzed by them are hydrolytic.

The use of alkali in aqueous solution leads naturally to another type of hydrolytic reaction, the *alkali fusion*, wherein the proportion of alkali is greatly increased and that of water correspondingly reduced.

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

followed by

$$2C_6H_5ONa + H_2SO_3 \rightarrow 2C_6H_5OH + Na_2SO_3$$

Quite a number of important preparations, such as that of β-naphthol, fall under this heading and may conveniently be classed as cases of hydrolysis, even though oxidation and reduction may be involved[1] and water plays but a minor part.

The line between hydrolysis and hydration is not very sharply drawn. The reaction

$$BaCl_2 + 2H_2O \rightarrow BaCl_2{\cdot}2H_2O$$

is surely hydration, whereas the saponification of a nitrile

$$C_2H_5CN + H_2O \rightarrow C_2H_5CONH_2$$

or the conversion of starch into glucose, whether wisely or not, has always been regarded as hydrolysis. For this reason, some interesting and important cases of hydration involving olefins and acetylene are included, regardless of consistency.

We may recognize, then, five types of hydrolysis:

1. Pure hydrolysis where water alone is used.
2. Hydrolysis with aqueous acid, dilute or concentrated.
3. Hydrolysis with aqueous alkali, dilute or concentrated.
4. Alkali fusion, with little or no water but at high temperatures.
5. Hydrolysis with enzymes as catalysts.

Still another classification would be to divide all cases of hydrolysis into

1. Those taking place in the liquid phase or phases.
2. Those taking place in the vapor phase.

Class 1 contains practically all cases of commercial importance, but interest in the vapor-phase reactions is growing. The passage of chlorobenzene vapor and steam at an elevated temperature over a solid catalyst to produce phenol and hydrochloric acid is an example of the latter type.

In this chapter, the subject matter will be presented as follows:

1. A brief review of the chief hydrolyzing agents.
2. A list of the materials susceptible to hydrolysis.
3. A discussion of the theory and mechanism of hydrolysis.
4. Equipment, materials of construction, etc., for hydrolysis.
5. Technical operations involving hydrolysis.

II. HYDROLYZING AGENTS

Although the word hydrolysis means decomposition by water, cases in which water unaided brings about *effective* hydrolysis are rare, and high temperatures and pressures are usually necessary even then. For complete and speedy reaction, an accelerating agent of some kind is nearly always indispensable, whatever the mechanism of its reaction may be. The most important of these are alkalies, acids, and hydrolyzing enzymes. A succinct survey of the use and peculiarities of these three agents, preceded by a list of cases in which water alone may be used, is given next.

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[1] FRY and BUTZ, *Rec. trav. chim.*, **52**, 129–138 (1933).

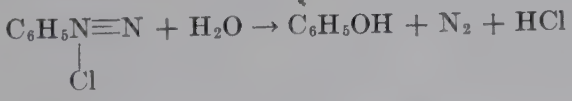
Water.—The Grignard reagent, so useful in synthesis, is hydrolyzed quickly and completely by water, as are the less manageable zinc alkyls and other organo-metallic compounds. The conversion of acetaldehyde into isopropyl alcohol by the Grignard reaction is a good illustration.

The acid anhydrides, lactones, lactides, and other internal anhydrides such as ethylene oxide are readily hydrolyzed by water alone, acetic anhydride reacting much more rapidly than either benzoic or phthalic. Mixed anhydrides, among which, for convenience, are included the acid halides, react with vigor, especially acetyl chloride, which is more reactive than acetic anhydride itself. In general, the stronger the two acids in these mixed anhydrides the more vigorous the hydrolysis; *e.g.*, acetyl chloride is more readily hydrolyzed than butyryl bromide. Benzoyl chloride, however, reacts with less readiness than acetyl chloride, despite the greater strength (dissociation) of benzoic acid. This is probably due to the lower solubility of benzoyl chloride in water.

Alkyl halides of complex composition react with water alone, though the simple halides like ethyl chloride are but slightly affected. Mustard gas, for example, probably owes some of its effect to the reaction

$$ClH_4C_2—S—C_2H_4Cl + 2H_2O \rightarrow HOH_4C_2—S—C_2H_4OH + 2HCl$$

which takes place fairly rapidly. Diazonium salts when heated with water hydrolyze completely.



$$\underset{\displaystyle Cl}{C_6H_5\overset{}{N}}\equiv N + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Phenol can thus be made, though not economically, from aniline. The alkyl sulfates, *e.g.*, ethyl hydrogen sulfate, hydrolyze when heated with water. Aronovsky and Gortner found that cooking poplar wood with water for 2 hr. at 100 lb. pressure (170°C.) dissolved out 20 per cent of the weight of the wood, part of the dissolved material no doubt resulting from hydrolysis.[1] The sodium salt of acetoacetic ester is completely hydrolyzed by water, as are the metallic alcoholates and a few other unimportant substances. A slight degree of hydrolysis seems to occur with numerous materials—esters, proteins, carbohydrates, etc.—especially upon boiling, but it should be emphasized again that water by itself is able to bring about complete and rapid hydrolysis of only very few substances. For all others, the intervention of a third reactant of some kind is required.

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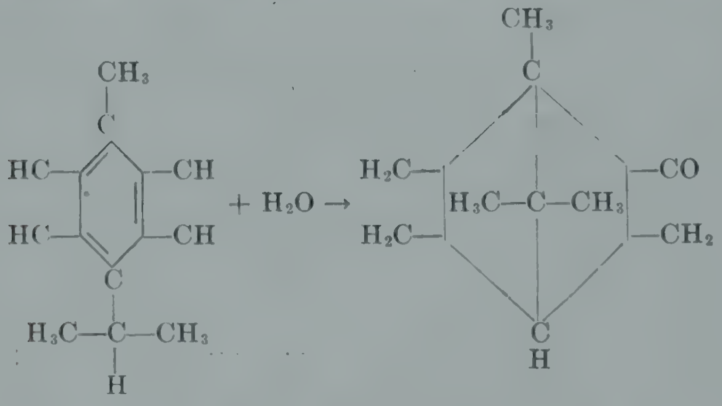
[1] Aronovsky and Gortner, *Ind. Eng. Chem.*, **22**, 264–274 (1930).

The use of steam instead of liquid water has brought results in a few cases. Benzenesulfonic acid with steam yields benzene and sulfuric acid

$$C_6H_5SO_3H + H_2O \text{ (steam)} \rightarrow C_6H_6 + H_2SO_4$$

and similarly α-naphthalenesulfonic acid hydrolyzes to naphthalene. Steam and chlorobenzene passed through porous silica at 575°C. give a 95 per cent yield of phenol, while similar results but with smaller yields have been obtained with other aryl and alkyl halides. The Twitchell (see page 690) and autoclave processes of making fatty acids from fats might almost be included, though both use a small amount of catalyst.

Camphor can be obtained by adding the elements of water to *p*-methylisopropylbenzene (*p*-cymene). The hydration is preferably carried out in the presence of a mercury salt and is promoted by the use of elevated temperatures and a lower alcohol as mutual solvent.[1] *p*-Cymene and water in a ratio of 2 parts to 1 by weight are dissolved in methanol, and the mixture refluxed for 60 hr. in the presence of mercuric sulfate. The crude product is a solution of camphor, methanol, and unconverted cymene. The hydration reaction, which involves the saturation of the three double bonds of *p*-cymene, may be expressed as follows:



Acid Hydrolysis.—In 1811, Kirchhoff observed that starch was transformed by aqueous mineral acids into glucose and showed that no acid was used up in the process. Braconnot, in 1819, hydrolyzed linen (cellulose) with strong sulfuric acid, obtaining a fermentable sugar. This use of acid in hydrolysis was rapidly extended to other classes of organic materials—the esters, sugars, amides, etc.—and it was found that wherever water brought about hydrolysis, acid accelerated the reaction. In addition, the latter seemed in many cases to initiate reaction where water alone failed. The acid hydrolysis of acetate esters has come to be a sort of proving ground for theories of catalysis. It is customary to attribute the effect of acid to the hydrogen-ion content' and, with dilute acid in many reactions, there is at least a rough proportionality between the velocity of reaction and the hydrogen-ion concentration. Like many other generalizations in chemistry, this relation is more honored in the breach than the observance, and, with concentrated acids, it does not hold at all. The undissociated acid and the negative radical have both been called upon from time to time to account for certain anomalous results.

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[1] Schwartz, U. S. 2,389,389 (1945).

Hydrochloric and sulfuric acids are naturally the most commonly used, though many others have been explored. Formic and trichloroacetic appear to be lower in activity than would be expected, whereas oxalic and benzenesulfonic are more active than sulfuric. Concentrations from very high to very low are used in both laboratory and commercial practice. The Bergius process for saccharifying wood employs 41 per cent hydrochloric, while the Scholler-Tornesch system, which is described later, uses 0.5 per cent sulfuric acid for the same purpose.

Sulfuric acid is particularly useful because it forms, with many types of organic substances, intermediate compounds that themselves readily undergo hydrolysis. This is exhibited in the acid process of fat splitting to make fatty acids—as well as in the similar Twitchell system—in making alcohol from ethylene, and probably also in the hydration of acetylene to make aldehyde. In all these, sulfuric acid exhibits a specific action, distinct from its hydrogen-ion concentration, and cannot be replaced by other acids.

The preparation of individual amino acids by the hydrolysis of proteins is generally very difficult because these natural materials are composed of some 20 amino acids having similar chemical properties. Generally, no one amino acid constitutes more than 10 to 20 per cent of the protein. Because of these inherent difficulties, the industrial production of amino acids from casein and soybean proteins awaits further progress in current research.

One protein that is used to the extent of about 10,000,000 lb. annually is wheat gluten—which is valued for its relatively high (35 to 40 per cent) content of glutamic acid, $HOOC(CH_2)_2CH(NH_2)COOH$. Monosodium glutamate is a condiment that is being used in increasing quantities for imparting a meatlike flavor to soups and other foodstuffs. The usual procedure for making monosodium glutamate involves hydrolysis of the gluten with a constant-boiling 20 per cent hydrochloric acid solution; removal of excess HCl by distillation; and filtration from humin followed by successive crystallizations of glutamic acid hydrochloride, glutamic acid, and monosodium glutamate in the presence of decolorizing carbon.[1]

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[1] OLCOTT, *Food Industries*, **16**, 541,576 (1944).

Although acid and alkali may frequently be used interchangeably on the same materials to give essentially the same products, this is not invariably true. The action of acid on acetoacetic ester and its derivatives leads to acetone, carbonic acid, and alcohol and its related products, while alkali on the same ester produces acetic acid and alcohol. Stieglitz has pointed out that the imido esters can be hydrolyzed by water in two distinct ways, depending upon whether the solution is acid or basic.[1]

Alkali Hydrolysis.—We may distinguish three different cases of hydrolysis with alkali:

1. The use of low concentrations of alkali in the hydrolysis of esters and similar materials: Here the hydroxyl ion is supposed to catalyze the reaction as the hydrogen ion does in catalysis by dilute acid. Since one of the products of reaction is usually an acid that reacts immediately with the hydroxyl ion, this case is of significance only in theoretical studies, where an instantaneous value of a reaction velocity is desired.

2. The use of sufficient caustic under pressure and in high concentrations to unite with all the acid produced;

$$C_6H_5Cl + NaOH\ aq. \rightarrow C_6H_5OH + NaCl + H_2O$$

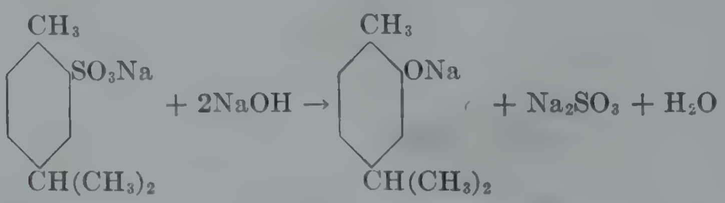
sometimes followed by

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

A variant of this is the passage of the vapors of chlorinated hydrocarbons mixed with steam over solid alkaline materials, such as lime, yielding alcohols.

$$2CH_3Cl + Ca(OH)_2 \xrightarrow{\text{Steam}} 2CH_3OH + CaCl_2$$

3. The fusion of organic materials with caustic soda or potash: This develops naturally from case 2 by decreasing the ratio of water. The formation of carvacrol from sodium *p*-cymenesulfonate is an example:



with, of course, the subsequent acidulation of the sodium salt.

This alkali fusion process is limited essentially to sulfonic acids, though the elimination of carbon dioxide is sometimes accomplished in this way.[2] Chlorinated and nitrated compounds do not seem to have been successfully subjected to this mode of treatment.

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[1] Stieglitz, *Am. Chem. J.*, **39**, 166 (1908).

[2] Phillips, *Ind. Eng. Chem.*, **13**, 759 (1921).

Alkali is used only to a limited extent in the hydrolysis of carbohydrates. Cellulose is rather resistant to alkali and, when attacked, is broken down but not distinctly hydrolyzed. The carbohydrates in corn cobs undergo deep-seated changes when heated at 240° with a concentrated caustic solution, oxalic and acetic acids being the principal products. When invert sugar is treated with two molar equivalents of sodium hydroxide—as a 50 per cent solution—lactic acid is obtained.[1] An aqueous solution of the sugar is added dropwise to the boiling caustic soda solution, and sodium lactate is obtained in yields of 67 per cent. The simplified reaction is:

$$C_6H_{12}O_6 + 2NaOH \rightarrow 2CH_3CHOHCOONa + 2H_2O$$

Caustic soda is the base most commonly used, but the alkali carbonates and bicarbonates as well as the alkaline-earth hydroxides all find occasional application. Potassium compounds show no advantage over the cheaper sodium materials, except that potassium hydroxide in some alkaline fusions permits the use of a lower temperature. Ammonium hydroxide and ammonium salts are rarely used.

Enzymatic Hydrolysis.—Comparatively few large-scale operations depend upon enzymes for hydrolysis. One or two enzymes (urease) are used for analytical purposes. Molasses is converted by invertase in the manufacture of industrial alcohol, and, of course, the whole brewing industry depends upon the complex hydrolysis of starch into maltose and glucose by the amylases. Despite its occasional industrial application, enzymatic hydrolysis is, however, primarily the concern of the biochemist.[2,3]

III. MATERIALS SUSCEPTIBLE TO HYDROLYSIS

There do not appear to be any general rules or far-reaching generalizations that will enable us to predict the behavior of organic materials toward hydrolyzing agents. For this reason, it is necessary to review one by one the chief types of compounds and to describe explicitly their behavior.

Hydrocarbons.—Saturated aliphatic hydrocarbons apparently do not suffer hydrolysis directly. There is no record of the reaction

$$C_nH_{2n+2} + H_2O \rightarrow C_nH_{2n+1}OH + H_2$$

taking place to the slightest degree, even with caustic or acid or enzymes or at high temperatures and pressures or any combination of these, nor has the reverse reaction been recorded. It is true that methane and steam have been converted into carbon monoxide and hydrogen and ultimately into carbon dioxide and hydrogen, by passage over a solid catalyst at an elevated temperature:

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[1] Lock, U. S. 2,382,889 (1945).

[2] Waldschmidt-Leitz, "Enzyme Actions and Properties," trans. and extended by R. P. Walton, John Wiley & Sons, Inc., New York, 1929.

[3] Gortner, "Outlines of Biochemistry," pp. 714–716, John Wiley & Sons, Inc., New York, 1929.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

but this would hardly be classed as hydrolysis. Hydrolytic rupture of the C—C bond occurs in many reactions of hydrocarbon derivatives such as chloral or acetoacetic ester with alkali.

With unsaturated hydrocarbons, the case is different. The reaction

$$C_nH_{2n} + H_2O \rightarrow C_nH_{2n+1}OH$$

has been effected on a large scale with ethylene, through the formation of an intermediate compound with strong sulfuric acid; even less difficulty is experienced with the homologues (propylene, butylene, etc.). The *direct* addition of water, without the aid of acid, has not yet been made practical. The reverse reaction whereby ethylene is made from alcohol vapor passed over a solid catalyst, such as alumina, is well known.

The addition of water to acetylene

$$C_2H_2 + H_2O \rightarrow CH_3CHO$$

whereby acetaldehyde and ultimately acetic acid are produced, has long been recognized and is today practiced on a large scale. Sulfuric acid containing either dissolved mercury sulfate or suspended mercuric oxide serves as the hydration catalyst.

This addition of water to the olefins and acetylene just mentioned takes place in the liquid phase. Benzene vapor when passed with steam through a hot quartz tube (650°C.) gives rise to detectable amounts of phenol:[1]

$$C_6H_6 + \underset{\text{Steam}}{H_2O} \rightarrow C_6H_5OH + H_2$$

This result has been confirmed by Lloyd, who obtained a conversion into phenol of 0.3 per cent of the benzene passed through the tube.[2] Various solid catalysts such as chromium oxide and zinc ferrite had little effect on the yield. The reverse reaction is practically complete.

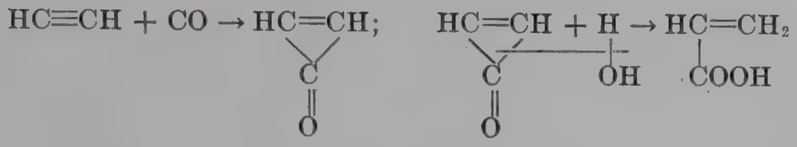
The preparation of acrylic acid from acetylene and carbon monoxide is considered here, although the hydration reaction is assumed to involve the addition of water to hypothetical cyclopropenone as shown below.[3]

[1] Fischer, *Ges. Abhandl. Kenntnis Kohle*, **5**, 417 (1920).

[2] Lloyd, Unpublished research.

[3] From a report presented at the 24th Kuko (Plastics Committee) meeting in Frankfurt am Main on Dec. 18, 1940, by Dr. Reppe, I. G. Farbenindustrie A-G. Translation by Callomon and Kline, *Modern Plastics*, **23**, 162 (1945).

The unstable cyclopropenone in combination with compounds having a labile hydrogen atom, such as water, alcohols, and amines, splits according to the equation presented above. When alcohols are employed in the reaction, the product will be the corresponding ester of acrylic acid.



$$HC{\equiv}CH + CO \rightarrow \underset{\underset{O}{\overset{\|}{C}}}{HC{=}CH};\qquad \underset{\underset{O}{\overset{\|}{C}}}{HC{=}CH} + \underset{OH}{H} \rightarrow \underset{COOH}{HC{=}CH_2}$$

Metal carbonyls are used as CO carriers, and, when the reaction is conducted in stoichiometric proportions, the presence of acids or halogens is necessary to bind the metal of the carbonyl as a salt. The mechanism of the process, using nickel carbonyl as CO carrier, may be represented as follows:

$$H_2O + C_2H_2 + \tfrac{1}{4}Ni(CO)_4 + \tfrac{1}{2}HCl\ aq. \rightarrow CH_2{=}CH{-}COOH + \tfrac{1}{4}NiCl_2\ aq. + \tfrac{1}{4}H_2$$

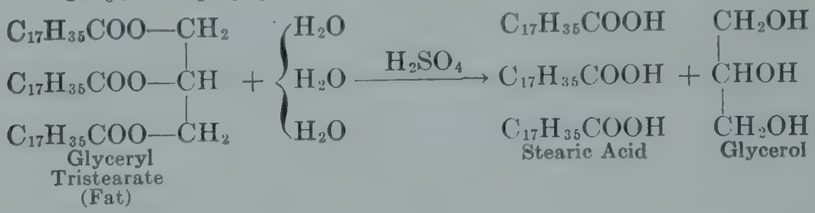
$$R{\cdot}OH + C_2H_2 + \tfrac{1}{4}Ni(CO)_4 + \tfrac{1}{2}HCl\ aq. \rightarrow CH_2{=}CH{-}COOR + \tfrac{1}{4}NiCl_2\ aq. + \tfrac{1}{4}H_2$$

Nickel carbonyl is the most suitable carrier, though cobalt carbonyl gives good results. Ordinary concentrated hydrochloric acid is preferred as a binder for the resultant nickel. Even at moderate temperatures (40 to 42°), the reaction is an extremely violent one and gives practically quantitative yields of acrylic acid or its derivatives when alcohols, amines, and mercaptans are used. The presence of water is necessary in preparing the acrylic acid esters; otherwise, propionic esters are formed to a considerable extent owing to the activity of the liberated hydrogen.

Carbohydrates.—Cellulose is hydrolyzed to glucose by acids and to cellobiose by its own specific enzyme cellulase. Alkali is not effective. Later on page 694, a detailed description of the large-scale saccharification of wood cellulose to glucose is presented. The 12-carbon sugars—sucrose, maltose, etc.—yield the corresponding monosaccharides on hydrolysis with enzyme or dilute acid, but alkali brings about other changes in them. Enzymes and dilute acids hydrolyze starch into maltose and glucose, whereas inulin yields only fructose by this treatment. Other carbohydrates, like pectins, xylan, and araban, suffer corresponding changes with acids or enzymes. It should be emphasized that alkalies are not, as a rule, useful with this class of substances.

Esters.—Organic esters of all kinds, including the esters of carbohydrates, are quite subject to hydrolysis with acids, bases, and, in many cases, enzymes. In this connection, the term *saponification* is commonly used instead of hydrolysis. The most important example is that of the saponification of fats and oils to make glycerol and either soap or fatty acids. All three common hydrolyzing agents find commercial application here, in the acid, the autoclave, and the enzymatic process of producing fatty acids. The decomposition of ethyl and methyl acetates by water plus a catalyst has probably received more attention than any other case of hydrolysis by reason of its bearing on the general subject of catalysis. Hydrolysis of esters is reversible, unlike that of the carbohydrates, so that the equilibrium point may be approached from both sides. The following equations represent typical cases of ester hydrolysis:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$$



$$\underset{\substack{\text{Glyceryl}\\\text{Tristearate}\\\text{(Fat)}}}{\begin{array}{l} C_{17}H_{35}COO{-}CH_2 \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO{-}CH \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO{-}CH_2 \end{array}} + \left\{\begin{array}{l} H_2O \\ H_2O \\ H_2O \end{array}\right. \xrightarrow{H_2SO_4} \underset{\text{Stearic Acid}}{\begin{array}{l} C_{17}H_{35}COOH \\ C_{17}H_{35}COOH \\ C_{17}H_{35}COOH \end{array}} + \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ \ | \\ CHOH \\ \ | \\ CH_2OH \end{array}}$$

The esters of inorganic acids, ethyl and methyl sulfates, ethyl hydrogen sulfate, the alkyl phosphates, glyceryl nitrate, etc., may all be hydrolyzed, generally speaking, by acids and bases.

Ethers (Organic Oxides).—Ether may be hydrolyzed to ethyl alcohol in the presence of a dilute aqueous acidic catalyst, such as 10 per cent sulfuric acid, at a temperature of 272°C., and under pressure of over 225 lb. per sq. in.[1] A 46 per cent conversion of ether to alcohol has been obtained at 275 to 300°C. and 120 atmos. pressure with aluminum oxide containing 5 per cent nickel oxide.[2] Secondary alcohols are more readily formed from ethers than primary. Ethylene oxide and trimethylene oxide hydrolyze fairly readily with water to form ethylene and propylene glycols, respectively. The higher polymethylene ethers are less reactive with water; the penta- and hexamethylene ethers have exceedingly stable ring systems, as is to be expected from the Baeyer strain theory. The addition of water to diphenyl oxide has been studied in connection with the production of phenol by the hydrolysis of chlorobenzene and is favored by a large excess of caustic alkali:

$$(C_6H_5)_2O + H_2O \xrightarrow{NaOH} 2C_6H_5OH$$

Hydrolysis of phenol and naphthol ethers with concentrated hydrochloric acid shows that meta derivatives decompose the least and para derivatives the most and that acidic groups increase the stability.[3]

Organic Halides.—These useful compounds differ markedly in their behavior toward hydrolyzing agents, the acid halides, like acetyl chloride, reacting readily with water alone, whereas varying degrees of resistance are shown by the alkyl and aryl compounds. Alcoholic solutions of caustic potash convert alkyl chlorides into the corresponding alcohols.[1]

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[1] U. S. 2,045,785 (1936).

[2] Balandin, Shuikin, Nesvizhskii, and Kozminskaya, *Ber.*, **65B**, 1557–1561 (1932).

[3] Kolhatkar and Ghaswalla, *J. Indian Chem. Soc.*, **8**, 511–516 (1931).

$$C_2H_5Cl + KOH\ (\text{alcohol}) \rightarrow C_2H_5OH + KCl$$

The hydrolysis of the amyl chlorides with sodium oleate and caustic soda solution to form the corresponding alcohols is the basis of a flourishing industry and is discussed on another page. The ease of removal of halogen increases markedly from chlorine to iodine and with increasing complexity of the compound. Ethylene chlorohydrin, for example, is easily and smoothly hydrolyzed to ethylene glycol by aqueous sodium bicarbonate:

$$CH_2OHCH_2Cl + NaHCO_3\ aq. \rightarrow CH_2OHCH_2OH + CO_2 + NaCl$$

A differentiation should be made between the hydrolysis of simple halogen compounds and chlorohydrins, since a difference in reaction mechanism, and in many cases a difference in order of magnitude of yield, is involved. Ethylene oxide is considered to be an intermediate between ethylene chlorohydrin and ethylene glycol.[2] The aromatic halides are much more difficult to hydrolyze. Acids are without effect upon them, save in the case of meta-chlorinated pyridine,[3] while in the Dow process for making phenol from chlorobenzene a pressure of 4,200 lb. and a temperature of 360°C. are required to make alkali effective. The presence of small amounts of copper speeds up this last reaction immensely but increases the relative proportion of by-products.

$$C_6H_5Cl + 2NaOH\ aq. \xrightarrow{Cu} C_6H_5ONa + NaCl + H_2O$$

Similar results have been reported for naphthol.[4] *p*-Chloronitrobenzene has likewise been commercially converted into *p*-nitrophenol by heating to 160°C. with aqueous caustic soda.

It has been found by Britton that when an aryl or alkyl-substituted aromatic halohydrocarbon is hydrolyzed at a relatively high temperature, *i.e.*, 300 to 400°C., in the absence of copper, there is formed a substituted phenol in which the hydroxyl group is in a position that is ortho or para to the original position of the halogen, together with a certain amount of the expected phenol.[5] For example, both *o*-phenylphenol and *p*-phenylphenol are prepared from *o*-chlorobiphenyl.

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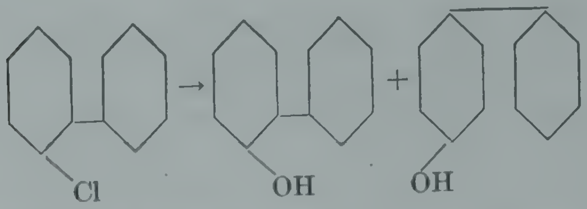
[1] GRANT and HINSHELWOOD, *J. Chem. Soc.*, **1933,** 258.

[2] SCHRADER, "The Glycol Industry," *Z. angew. Chem.*, **42,** 541–546 (1929).

[3] U. S. 1,778,784 (1930).

[4] U. S. 1,882,825, 1932; 1,992,154 (1935).

[5] U. S. 1,996,744 (1935).



The hydroxy compounds are not convertible into isomers by treatment with alkalies in like manner. Similar results were obtained in the production of naphthols from bromo- and chloronaphthalenes.[1]

Nitrogen Compounds.—Aliphatic and aromatic amines—ethylamine and aniline—resist hydrolysis even under extreme conditions, though the production of α-naphthol from α-naphthylamine under pressure is recorded.[2] 1-Naphthol-4-sulfonic acid is produced by a "reverse Bucherer reaction" by the hydrolysis of naphthionic acid with bisulfite.[3] Amides are hydrolyzed to the ammonium salt of the corresponding acid when heated with water, but, in the presence of acids and bases, there is a marked increase in the rate of hydrolysis.

$$CH_3CONH_2 + H_2O \rightarrow (CH_3COOH + NH_3) \rightarrow CH_3COONH_4$$

The hydrolysis of two fairly important nitrogenous sweetening substances—dulcin and saccharin—has been minutely studied by Täufel and associates.[4] Dulcin (*p*-phenetylcarbamide) in strongly acid or alkaline solution is converted to ammonia and *p*-phenetylcarbamic acid, but in boiling water more complicated changes occur. The conclusion is drawn that this material, when used for sweetening purposes, should be added *after* cooking. Saccharin boiled in neutral water does not hydrolyze appreciably but in alkaline media changes to *o*-sulfoamidobenzoic acid, while acid catalysts carry the hydrolysis farther to the ammonium salt. A temperature of 100°C. in the foodstuffs to which it is added does not cause appreciable hydrolysis.

Nitriles undergo a fairly complete but peculiar form of hydration when heated with water, especially if alkali or acid be present. Thus, the hydrolysis of ethyl cyanide does *not* proceed as follows:

$$C_2H_5CN + H_2O \rightarrow C_2H_5OH + HCN$$

instead, the bond between the carbon and nitrogen is broken, and we have

$$C_2H_5CN + 2H_2O \rightarrow C_2H_5COONH_4$$

Benzonitrile acts in a similar way to form benzoic acid but requires sulfuric acid in the reacting mixture.

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[1] U. S. 1,996,745 (1935).

[2] Ger. 74,879 (1892); Vorozhtzov and Gutorko, *J. Gen. Chem.* (*U.S.R.R.*), **5,** 1581 (1935).

[3] U. S. 1,880,701 (1933).

[4] Täufel, *Z. Elektrochem.*, **34,** 115–127; 281–291 (1928).

Isocyanides are stable toward alkalies but hydrolyze in the presence of acids to form an acid and an amine:

$$CH_3NC + 2H_2O \rightarrow CH_3NH_2 + HCOOH \rightarrow H{\cdot}COONH_3CH_3.$$

Nitro compounds, like nitrobenzene and nitromethane, are not readily hydrolyzed. Indeed, nitroethane may be distinguished in this way from ethyl nitrite, which hydrolyzes readily with caustic alkali:

$$\underset{\text{Ethyl Nitrite}}{C_2H_5ONO} + NaOH \rightarrow C_2H_5OH + NaNO_2$$

Sulfonic Acids.—The sulfonic acids require rather drastic methods of hydrolysis. The aliphatic members of the group do not hydrolyze; *e.g.*, ethylsulfonic acid ($C_2H_5SO_3H$) may be boiled with caustic soda solution or with concentrated acids without decomposition, whereas the ester ethyl hydrogen sulfate hydrolyzes readily:

$$C_2H_5OSO_3H + H_2O \rightarrow C_2H_5OH + H_2SO_4$$

Benzenesulfonic acid, when treated with steam under pressure, yields benzene and sulfuric acid:

$$C_6H_5SO_3H + \underset{\text{Steam}}{H_2O} \rightarrow C_6H_6 + H_2SO_4$$

but, when fused with caustic soda, sodium phenoxide is the product:

$$C_6H_5SO_3H + 3NaOH \xrightarrow{\text{Fusion}} C_6H_5ONa + Na_2SO_3 + 2H_2O$$

The action of steam on α-naphthalenesulfonic acid similarly yields naphthalene. Practically all aromatic sulfonic acids may be hydrolyzed with mineral acids to the parent hydrocarbons, but each sulfonic acid requires a specific minimum temperature. α-Naphthalenesulfonic acid hydrolyzes at a much lower temperature than the beta compound. However, the β-compound with fused caustic acts quite like the corresponding benzenesulfonic acid to give β-naphthol, sodium sulfite, and water. Under certain conditions, steam may replace the more expensive fused caustic alkalies in the hydrolysis of aromatic sulfonates that are volatile with steam:[1]

$$RSO_3M + ROM + H_2O \rightleftharpoons M_2SO_3 + 2ROH$$

The reaction involves hydrolysis of the alkali sulfonates in the presence of the phenoxide at temperatures corresponding to those employed in alkali fusions, *viz.*, 350 to 400°C. To avoid difficulties in agitation, an excess of the phenoxide is employed. The accumulated sulfite is removed by diluting the reaction mass and filtering while hot. The condensed vapors yield a 20 to 30 per cent phenol suspension.

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[1] U. S. 1,992,167 (1935).

IV. THEORY AND MECHANISM OF HYDROLYSIS

The preceding part of this chapter has dealt with the reagents of hydrolysis and the behavior of the organic materials undergoing the reaction. The mechanism of the hydrolytic process is now to be studied as well as the various factors that influence its course. In liquid-phase hydrolysis, the reaction mechanism has usually been viewed as a special case of the general question of homogeneous catalysis, and the two classic examples of organic hydrolysis—saponification of esters and inversion of sucrose—have been favorite proving grounds for the numberless theories advanced in this field. A brief discussion of these reactions should serve to set forth the past and present status of hydrolytic mechanism in the liquid phase, especially from the "ion" point of view. In view of the diverse materials that undergo hydrolysis, it is too much to expect any single far-reaching generalization, unless it should refer to some peculiar property of water.

Hydrolysis of Esters.—The early investigators recognized that esters of the organic acids were partially hydrolyzed by water alone but that the reaction was very slow and did not go to completion. The addition of almost any acid speeded up the reaction immensely but scarcely shifted the equilibrium point, while the addition of a base likewise quickened the rate, and, if enough were added to neutralize wholly the acid formed, the reaction was carried to completion.[1] The accelerating effect of the acid, since it could not be attributed to the neutralization of a product, obviously required another explanation. Since hydrogen alone is common to all acids and to water, it was natural to attribute the catalyzing effect to it. However, the acceleration due to different acids did not prove to be proportional to the hydrogen added by them to the solution, so that when the appearance of the Arrhenius dissociation theory afforded an opportunity to distinguish between *active* (dissociated) and *inactive* (combined) hydrogen, it did not take long to discover that, for dilute acids at least, the acceleration was roughly proportional to the active hydrogen, or *hydrogen-ion concentration.* No very definite ideas were advanced at this time as to the exact way in which the hydrogen ions acted, whether by impact or by intermediate compound formation or otherwise.

Deviations from even this rough proportionality were soon found with dilute as well as concentrated acids, and the next step was to assume the existence of two kinds of hydrogen ion—unhydrated (active) and hydrated (inactive)—only the former having catalytic properties.[2] Finally, Karlsson, in an illuminating paper, finds it even necessary to assume that hydrogen ions, hydroxyl ions, undissociated acid, and neutral salt all catalyze materially the hydrolysis of esters.[1]

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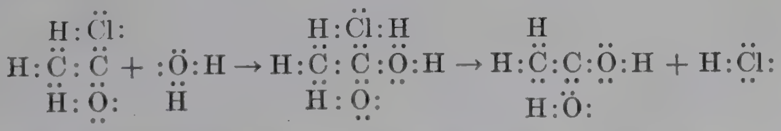
[1] See chapter on Esterification.

[2] LAPWORTH, *J. Chem. Soc.*, **107**, 857 (1915); RICE, *J. Am. Chem. Soc.*, **45**, 2808 (1923).

These results, disconcerting as they are in the light of the original pronouncement of Ostwald and Arrhenius that hydrogen ions alone were effective in ester catalysis, are brought somewhat into line again by Brönsted's broadening of the definition of the terms *acid* and *base* and his assumption that uncombined (unhydrated) hydrogen ion cannot exist in aqueous solution, that ordinary hydrogen ion is H_3O^+. If we accept his definition of an acid as a *proton donor* and of a base as a *proton acceptor*, we can include under the terms acid and base all the substances so far found to catalyze ester hydrolysis and can state that only acids and bases, as newly defined, catalyze this reaction.

In interpreting the electronic behavior of water, it is necessary to recall that both acids and oxidizing agents are electrophilic (gain electrons), which is to be expected from the Lewis theory; *i.e.*, acids accept a share in an electron pair whereas oxidizing agents gain electrons outright.[2] Conversely, bases and reducing agents are electrodotic (lose electrons). Water acts as an acid toward ammonia, as a base toward hydrogen chloride, as an oxidizing agent toward active metals, and as a reducing agent toward fluorine. Water not only is amphoteric but is both an oxidizing and a reducing agent. Acetyl chloride reacts with water in a typically acid fashion. Thus, the carbonyl group accepts an electron pair from the oxygen of water:



$$\begin{array}{ccccccc}
\mathrm{H:\ddot{C}l:} & & & \mathrm{H:\ddot{C}l:H} & & \mathrm{H} & \\
\mathrm{H:\underset{\cdot\cdot}{\ddot{C}}:\ddot{C}} + & \mathrm{:\underset{\cdot\cdot}{\ddot{O}}:H} & \rightarrow & \mathrm{H:\underset{\cdot\cdot}{\ddot{C}}:\ddot{C}:\underset{\cdot\cdot}{\ddot{O}}:H} & \rightarrow & \mathrm{H:\underset{\cdot\cdot}{\ddot{C}}:\underset{\cdot\cdot}{C}:\underset{\cdot\cdot}{\ddot{O}}:H} & + \ \mathrm{H:\underset{\cdot\cdot}{\ddot{C}l}:} \\
\mathrm{H:\underset{\cdot\cdot}{O}:} & \mathrm{H} & & \mathrm{H:\underset{\cdot\cdot}{O}:} & & \mathrm{H:\ddot{O}:} &
\end{array}$$

The growing complexity of the subject and the appalling amount of data already assembled make it necessary to reduce the treatment here to a few categorical statements, to most of which exception can probably be taken. Even if these statements are correct for ester hydrolysis, it is questionable how far they apply to hydrolysis of other types of substances:

1. Hydrogen ions are chiefly responsible for accelerating acid hydrolysis of esters of weak (organic) acids, such as methyl acetate.

2. Hydrogen ions do *not* catalyze the hydrolysis of esters of strong (mostly inorganic) acids—phosphoric, sulfuric, nitric, benzenesulfonic, trichloroacetic.[3]

3. Proportionality between the rate of reaction and the hydrogen-ion concentration is usually approximate only. Since hydrogen ions cannot be supplied without corresponding negative ions, the deviations find an

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[1] Karlsson, *Z. anorg. allgem. Chem.*, **145**, 1–57 (1925).

[2] Luder, *J. Chem. Ed.*, **19**, 24–26 (1942); **22**, 304 (1945).

[3] Olivier and Berger, *Rec. trav. chim.*, **41**, 637 (1922).

easy but futile explanation in the assumed effect of the latter or even of the undissociated molecule.[1]

4. Little evidence of the existence of intermediate compounds between water, the ester, and the hydroxyl ions has been presented, though such compounds have repeatedly been postulated, and elaborate calculations based upon their presence made.

The above points have to do chiefly with acid hydrolysis. There is unimpeachable evidence that hydroxyl ions, and indeed all bases defined according to Brönsted, catalyze the hydrolysis of esters. Wijs showed that the rate of hydrolysis of methyl acetate in pure water was proportional to the sum of the concentrations of the hydrogen and the hydroxyl ion.[2] The exact relationship between hydroxyl ion and reaction velocity is, of course, clouded by the shift in the equilibrium point due to the removal by alkali of the acid produced in the reaction. This difficulty is not encountered with acids.

The preceding discussion of acid and base hydrolysis, which applies specifically to esters, may be extended to most cases where dilute acids or alkalies appear as catalysts at moderate temperatures. It has no application to hydrolysis with concentrated acids and alkalies at high pressures and temperatures and, of course, none to alkali fusion. Since most commercial applications of hydrolysis fall in the latter classes, we cannot expect much application of theory to practice.

Effect of Temperature on Hydrolysis.—Temperature changes influence hydrolytic reactions, as they do most others, in two ways, by shifting the equilibrium point and by changing the rate of reaction. Very little has been published on the former point, but no doubt the general relationship connecting the heat of the reaction, the equilibrium constant, and the temperature is valid here, as elsewhere:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant, ΔH the heat absorbed, and T the absolute temperature. Expressed qualitatively, if the hydrolytic reaction is accompanied by an evolution of heat, it will proceed farther at low temperatures, and *vice versa*. In commercial processes, the necessity of completing the operation in a minimum of time has led to the use of the highest temperatures practicable in order to take advantage of the greater speed of reaction, regardless of the possibly unfavorable shift of the equilibrium point. A mixture of equivalent amounts of ethyl acetate and steam kept in contact with silica gel gave the following figures:

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[1] BATES and TAYLOR, *J. Am. Chem. Soc.*, **49**, 2444 (1927); **51**, 771 (1929).

[2] WIJS, *Z. physik. Chem.*, **12**, 514 (1893).

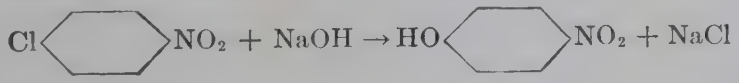
°C.	% Hydrolyzed
At 150	15.3
200	16.7
250	21.7
300	25.1

Evidently, the hydrolysis in this case is endothermic.

More important than the effect upon the equilibrium point is the influence of temperature upon the speed of reaction. Hydrolytic reactions, like most others, follow the rule that the rate doubles approximately for every 10° rise in temperature. For the temperature interval 25 to 35°C., the hydrolysis of ethyl acetate, formylacetic acid, and ethylcyanoacetate shows a rate increase of 2.4; the acid hydrolysis of amides, 3.4; and cane sugar inversion, 4. For this same temperature interval, the rate of hydrolysis of organic acid anhydrides increases 1.84 times. Enzymatic hydrolysis does not differ in this respect materially from that produced by other catalysts, but only a small temperature range has been covered. Values as high as 5.3 for trypsin and as low as 1.2 for lipase are recorded. The rapid destruction of enzymes at temperatures over 60°C. complicates this case. The fact, however, that their temperature coefficients are of the same order of magnitude as those for acids and bases is of importance in arriving at a correct idea of enzyme action.

The general effect of the operating temperature in a case of industrial hydrolysis is brought out in the following table, which gives the results obtained by heating *p*-chloronitrobenzene for 12 hr. with four times its weight of caustic soda in aqueous solution, to form *p*-nitrophenol:

TABLE I.—EFFECT OF TEMPERATURE: HYDROLYSIS OF *p*-CHLORONITROBENZENE



Temp., °C.	Conc. NaOH, %	Chloronitrobenzene recovered, %	Nitrophenol yield, %
120	15	91.2	8.8
140	15	2.3	90.6
160	15	Trace	74.6

Evidently, the rate of reaction at 120°C. is far too slow, though no waste of material occurs, whereas at 140°C. the rate is much faster, and only 7 per cent of the starting material is destroyed. Either the temperature 160° is too high, or the heating is continued too long, since one-fourth of the raw material is lost. Actually the proper time of heating is about 4 hr., and 160°C. is a suitable temperature.

Figure 1 illustrates the relation between temperature and time of heating necessary to secure a 92 per cent yield of phenol from chlorobenzene and aqueous caustic.[1] At 370°C., 12 min. is sufficient; at 295°C., 3 hr.

Few data have been published dealing with the effect of temperature on vapor-phase reactions, other than the ethyl acetate hydrolysis already discussed. Unpublished experiments by Lloyd show that the rate of formation of phenol from chlorobenzene and steam in the presence of silica gel is negligible at 350°C. but exceedingly rapid at 575°C.

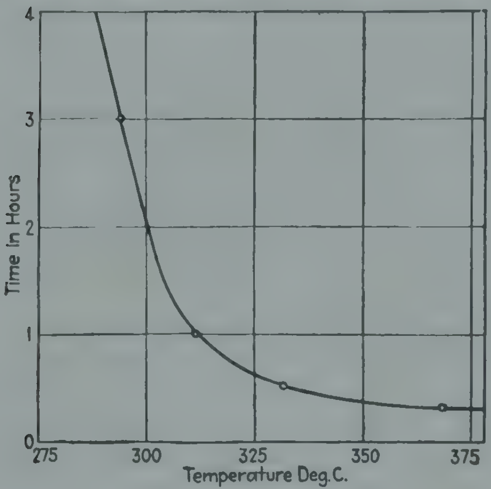


FIG. 1.—Relation between the temperature and the time necessary to secure a 92 per cent yield of phenol from chlorobenzene and aqueous caustic.

Effect of Concentration of Reactants.—Increase in the concentration of the hydrolyzing reagent would naturally be expected to speed up the reaction, other things being equal, but a high concentration sometimes leads to undesirable byproducts. In the reaction just mentioned, hydrolysis of chlorobenzene, a quick and fairly complete conversion of chlorobenzene to phenol is effected by a very high caustic concentration, but the production of tar is greatly increased also. The following table, which relates to the production of *p*-nitrophenol from *p*-chloronitrobenzene, shows the relation among reaction times, yields, and reagent ratios for this particular case:

TABLE II.—EFFECT OF NaOH CONCENTRATION: HYDROLYSIS *p*-CHLORONITROBENZENE
Temperature, 160°C.

Ratio NaOH to halide	Conc. NaOH %	Time, hr.	Halide recovered	Phenol yield, %
2:1	15	4	41.8	53.7
3:1	15	4	17.17	80.1
4:1	15	4	Trace	99.8
3:1	20	4	0.4	99.5
4:1	20	4	Trace	98.4
2:1	15	6	36.0	55.1
3:1	15	6	14.9	73.0
4:1	15	6	Trace	99.5

Catalysts.—It will be convenient to divide the large number of catalysts included under a broad definition of the term into two classes:

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[1] HALE and BRITTON, *Ind. Eng. Chem.*, **20,** 117 (1928).

(1) materials that are present in large amounts and that in some cases react with one of the products, like caustic soda in the Dow phenol process or hydrochloric acid in the Bergius wood saccharification method, and (2) substances present in small amounts, like sulfuric acid in the Scholler-Tornesch saccharification process or hydrochloric acid in the making of glucose from starch. Acids and bases may fall into both classes; enzymes are confined to the latter. The necessity of cataloguing hydrogen and hydroxyl ions is avoided by adopting Brönsted's definitions of the terms acid and base. In addition to these more or less general catalysts, there are a few specific ones such as quinine, sodium oleate, manganese sulfate, and small amounts of copper salts, the last being especially useful in the hydrolysis of aromatic halides. Mercuric oxide along with sulfuric acid promotes the hydration of acetylene, while ultraviolet light[1] hydrolyzes aqueous acetone to methane and acetic acid. Finely divided charcoal and platinum as well as stannous chloride have also found application.

These are mostly cases of homogeneous catalysis, in the liquid phase. The passage of steam along with the vapor of the substance to be hydrolyzed, both in the vapor phase, over and through an activating solid, has introduced another set of catalysts. To hydrolyze esters in this way, the oxides of titanium, thorium, and silicon (silica gel) have been largely used. In the vapor-phase hydrolysis of aromatic halides, silica gel, titania, thoria, and iron-free alumina in as porous a form as possible have been used, while patent claims also cover the use of metal phosphates and silica gel impregnated with phosphoric acid. Here, again, the presence of a little copper in some form, in the silica gel, is an improvement.

Reversibility.—Many hydrolytic reactions, including the decomposition of esters, are reversible, but others, such as sucrose inversion and protein hydrolysis, though not necessarily complete, have not been reversed. In this respect, they differ not at all from reactions in general. It has been definitely shown that hydrolyzing enzymes catalyze in both directions and are capable of synthesizing natural products, notably the glucosides.

Vapor-phase Hydrolysis.—The preceding treatment of the theory and mechanism of hydrolysis has dealt almost altogether with reactions in the liquid phase or phases. Enzymatic hydrolysis, however, probably constitutes a two-phase system predominantly liquid; in certain commercial processes, we have hydrolysis taking place at the intersurface of emulsions. A few vapor-phase hydrolytic reactions have come to light of late years in addition to the well-known hydrolysis of esters, and considerable interest is apparent in this field. Such reactions afford good examples of heterogeneous catalysis, as they take place at the surface of a solid catalyst. The hydration of acetylene may be regarded as a connecting link between the liquid- and vapor-phase group.

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[1] QURESHI and TAHIR, *J. Phys. Chem.*, **36**, 2670–2673 (1932).

V. CONSTRUCTION AND CONTROL OF EQUIPMENT FOR HYDROLYSIS

Materials of Construction. General.—If the examples of commercial hydrolysis later described be examined carefully, it will be seen that they take place, without exception, either in acid or in alkaline media. The acids used are confined to sulfuric or hydrochloric; the bases include caustic soda or potash and the alkaline salts of weak acids. The acids may be dilute or concentrated; the bases, aqueous or fused. It is obvious that different materials of construction are required for these different cases. Alkaline processes have, in general, the great advantage that with rare exceptions, they may be carried out in iron or steel vessels. Only in exceptional cases do we find caustic soda attacking iron to produce hydrogen. In general, no great difficulties are encountered with materials of construction in alkaline hydrolysis. Even the severe treatment experienced by the cast-iron pots used foı caustic fusion does not shorten their life so much as might be expected.

Only two acids—sulfuric and hydrochloric—require consideration under acid hydrolysis. Until the advent of Duriron (high-silicon iron), lead-lined equipment was essential for all processes in which sulfuric acid was used, except for very concentrated acid. Saccharification of wood with very dilute sulfuric acid takes place in lead-lined or refractory brick apparatus, while the absorption of olefins requires acid of specific gravity 1.84, and lead-lined containers are not needed. The hydrolysis of the resulting sulfate, whereby dilute acid is produced, must be conducted in lead equipment, which may further be protected by close-fitting Pyrex glass bricks. Duriron is successfully used in acetylene hydration, where dilute sulfuric acid is encountered, but it is not so adaptable or easily fabricated as lead.

Hydrochloric acid as a hydrolyzer and as a product of hydrolysis in the absence of alkali has been the source of much trouble. It is one of the most corrosive chemicals known. However, even at slightly elevated temperatures, perfectly dry hydrogen chloride gas has very little corrosive action and is easily handled in iron equipment. Nickel and monel metal are fairly resistant to low hydrochloric acid concentrations. With dilute acid, several of the copper base alloys, such as phosphor bronze, aluminum bronze, manganese bronze, and Everdur metal, have fairly good resistance and can often be used in applications where corrosion can be offset by a heavy wall thickness. A general penetration rate for good resistance is below 10×10^{-6} cm. per day.[1] Many nonmetallic materials of construction, such as rubber, stoneware, fused silica, glass, and plastic materials such as Tygon and Proflex, have excellent resistance to hydrochloric acid.

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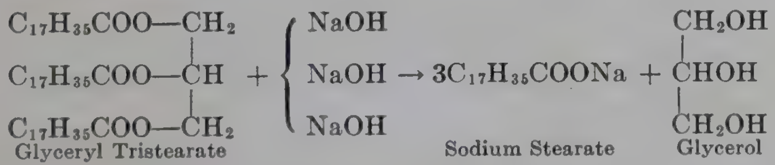
[1] DURGIN, LUM, and MALOWAN, *Trans. Am. Inst. Chem. Eng.*, **55**, 643 (1937).

In the laboratory, glass and silica are, of course, satisfactory, but their use is limited in commercial work. The starch-glucose transformation takes place in an acid concentration of less than 1 per cent and at low temperature, so that bronze and copper metal containers suffice. The Bergius wood saccharification method uses superconcentrated hydrochloric acid (40 per cent) and makes extended use of stoneware and of iron lined with acid-resisting tiles joined by a special cement. Rubber-lined iron is also used in the evaporator required for this process. The difficulty of handling wet hydrochloric acid gas has been one of the retarding factors in the development of vapor-phase hydrolysis of organic halides, but the use of tantalum is finding favor in continuous processes involving large production. The discovery that Toncan metal (an alloy of iron, molybdenum, and copper) is preferentially wetted by an organic material rather than by aqueous acid and is therefore much less subject to corrosion may be of significance.[1] An iron-nickel-molybdenum alloy (Hastelloy A) shows similar properties.

VI. TECHNICAL OPERATIONS INVOLVING HYDROLYSIS

Soap, Glycerol, and Fatty Acids.—Oils and fats are glycerol esters of fatty acids, saturated and unsaturated. By hydrolyzing these fats with steam or acid or enzymes, we obtain the glycerol and organic acid directly; if we add caustic soda to the water in hydrolyzing, common soap results instead of the fatty acid.



$$\begin{array}{l} C_{17}H_{35}COO{-}CH_2 \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO{-}CH \\ \qquad\qquad\quad | \\ C_{17}H_{35}COO{-}CH_2 \end{array} + \left\{ \begin{array}{l} NaOH \\ NaOH \\ NaOH \end{array} \right. \rightarrow 3C_{17}H_{35}COONa + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Eighty per cent of our soap is made through the process described by the above equation. In ordinary soapmaking, the fats are placed in a large steel pan (kettle) provided with a perforated steam coil; steam is blown in until the resulting liquid is heated to 80°C.; and some water from the condensed steam appears at the bottom of the kettle. Caustic soda is then gradually added, while live steam keeps the mass stirred and emulsifies it. At this stage, one of the three acid radicals combined with the glycerol is removed. More alkali is added, and the boiling with steam continued until the solution of soap is pasty, a condition indicating that the second acid radical has been properly hydrolyzed off from the glycerol. Salt is added to the mass at the proper time to salt out the soap that rises to the top, while the salty aqueous solution containing glycerol settles to the bottom and may be drawn off. More alkali is now added, and boiling renewed, and the soap again salted out. This operation may be repeated to ensure complete hydrolysis of the fat, or as often as desired, depending upon the nature and quality of soap desired. Finally the pan is covered, to retain the heat, and the contents separated into three layers, of which the top is good soap. This layer is skimmed off and put in frames to solidify.

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[1] AYRES, *Trans. Am. Inst. Chem. Eng.*, **22**, 23 (1929).

Not only in its manufacture but in its use does soap involve hydrolysis. Like other salts of strong bases and weak acids, sodium stearate and the other sodium soaps spontaneously hydrolyze somewhat in water, and upon this hydrolysis to some extent depends the detergent (cleansing) effect of soap.

Fatty Acids.—The above process is the natural and direct one by which to make soap, but if the fatty acids are wanted, for candlemaking and other purposes, the use of alkali must be avoided unless subsequent treatment with acid at additional expense is to be incurred. For these fatty acids, four distinct processes are available. In one—the autoclave method—1 to 3 per cent of lime or magnesia or zinc oxide is added to the fat or oil in an iron autoclave, and the mixture agitated with steam at 8 to 10 atmos. for 6 to 8 hr. The fatty acids rise to the top of the mass, and the aqueous glycerol extract remains below. The oxide added acts as a catalyst but ultimately combines with some of the fatty acid and must be removed by the subsequent addition of sulfuric acid. The higher the pressure employed the lower need be the amount of oxide used.

In the *acid* process for fatty acids, the dehydrated fat is violently churned up for 30 min. with 4 to 6 per cent of 66°Bé. sulfuric acid, producing a black mixture of *sulfonated* fat. No hydrolysis has taken place up to this point. This black mixture is now boiled with water, which accomplishes the hydrolysis, the fatty acids as usual rising to the surface and leaving the acidic glycerol solution underneath. This acid method has the advantage of converting any oleic acid (liquid) in the fats into isooleic (solid), thereby increasing the total yield of desirable solid acid.

Since oil or liquefied fat is insoluble in water, two liquid phases exist during hydrolysis, and the reaction rate, of course, depends upon their surface of contact—the greater the surface the faster the saponification. The best way to secure a large surface of contact between two liquids is to emulsify them thoroughly. For example, although pure glycerides react slowly with caustic, the soaps produced from the free fatty acids in commercial soap stocks promote emulsification, thereby increasing the rate of reaction. Twitchell discovered that a small amount (2 per cent) of a sulfo-aromatic compound added to the system produced such an excellent emulsion that a current of steam without any mineral acid or base effected complete saponification. In this Twitchell process (Fig.

2), the fat is first freed from foreign matter by boiling in a lead-lined tank with dilute sulfuric acid and is then transferred to a second lead-lined tank with a close-fitting cover. After the addition of one-third its weight of water, the mixture is treated with 1.0 per cent of the Twitchell reagent and heated with live steam for 24 hr. Ninety per cent of the fatty acids is set free in this time. The glycerol-water lower layer is drawn off, and the fatty acids that have risen to the surface are boiled again with fresh water for 12 hr., and the separation repeated. Low-grade fats and greases can be effectively treated in this way. Twitchell's reagent may be made by adding concentrated sulfuric acid to benzene and oleic acid, while the temperature is kept below 30°C.

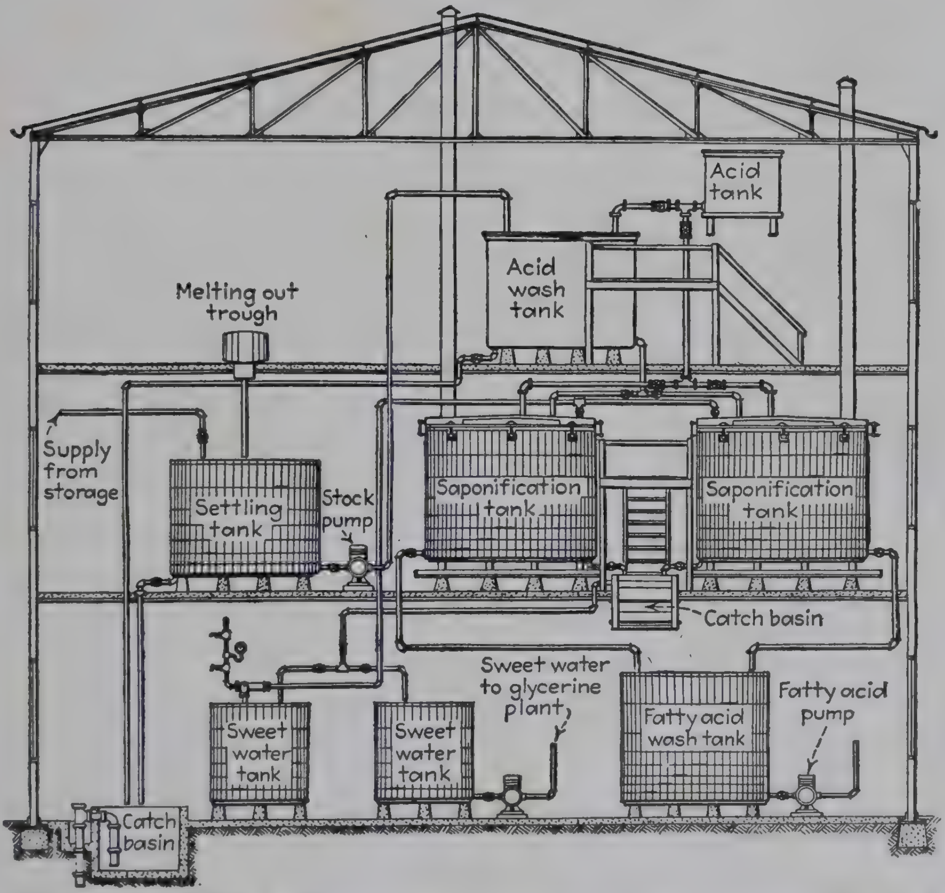

Acid tank
Acid wash tank
Melting out trough
Supply from storage
Settling tank
Stock pump
Saponification tank
Saponification tank
Catch basin
Sweet water to glycerine plant
Fatty acid pump
Fatty acid wash tank
Sweet water tank
Sweet water tank
Catch basin

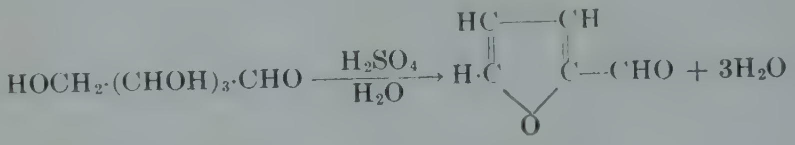
FIG. 2.—Twitchell process fat-splitting plant, with settling tank, two saponification tanks sweet-water tanks, and fatty-acid wash tank. (*Wurster and Sanger, Inc., Chicago.*)

$$C_6H_6 + C_{17}H_{33}COOH + H_2SO_4 \rightarrow C_6H_4(SO_3H)(C_{17}H_{35}COO) + H_2O$$

Glycerol.—From all these different processes for hydrolyzing fats into soap or fatty acids, glycerol is recovered and refined for the various purposes to which it is now applied. Practically all glycerol refining is now accomplished by distillation with steam under diminished pressure.

Hydrolysis of Carbohydrates.—The chief carbohydrates are th sugars, cellulose, and starch with its related polysaccharides. Of these the only ones hydrolyzed in large-scale industrial operations are th pentoses, from which furfural is obtained, and starch, from which glucos is produced.

Furfural.—The commercial production of furfural depends on th conversion of the pentosans of oat hulls and other cereal products. Usin xylose as an example, the hydrolytic reaction may be represented a follows:



Ordinarily, oat hulls, which have a relatively high pentosan content an which are available as a by-product of cereal manufacture, are used During the war, however, the need for furfural was greatly increase because of its use in the extraction of butadiene from petroleum dehydrogenation operations. As a result, corn cobs, rice hulls, and cottonsee bran were extensively employed. The yields of furfural per 100 lb. o such pentoses-containing materials on a dry basis are closely as follows:

	Pounds
Rice hulls	7.5
Corn cobs	11.0
Cottonseed bran	12.5
Oat hulls	13.5

The raw materials are conveyed from storage, loaded into rotatin digesters together with dilute (5 to 10 per cent) sulfuric acid, and cooke under 50 to 100 lb. steam pressure for approximately 2 hr. The furfura that is formed is carried out by the steam when the digester pressure i released and is separated by distillation and then further purified by fractional distillation. Methanol is separated from the furfural and is sold a a by-product. Acetic acid produced in small amounts is not recovered The residue from the digesters is either burned to produce steam for th plant or is sold as a conditioner for fertilizers. Approximately 1.5 lb. o sulfuric acid is consumed per 100 lb. of material treated.

Hydrolysis of Starch—In Germany, starch is derived principall from potatoes (Irish); but in the United States, it is obtained almos exclusively from Indian corn (*Zea Mays*).[1] The latter process include the following steps:

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[1] The production of starch from sweet potatoes is now being successfully conducte on a plant scale: the process being based on the research of the Bureau of Agricultura and Industrial Chemistry, U. S. D. A.

1. The clean corn grain is soaked or steeped for 1 or 2 days in warm water containing 0.25 per cent sulfur dioxide, the latter to keep the mixture sweet. This process is carried on in large hopper-bottomed steeping vats, capable of holding 2,500 bu. each. By means of steam syphons, the water is kept in circulation and at the same time maintained at a temperature between 46 to 52°C. (115 to 125°F.). In some plants, a battery steeping system in which fresh water passes successively from the most thoroughly steeped to the fresh grain has supplanted the above.

2. The softened grain is torn apart in attrition mills and transferred to the separators—huge cast-iron vats, in which the germ rises to the surface and is separated continuously from the ground corn and starch milk.

3. The bran is retained on the surface of silk sieves through which the mass is filtered.

4. The starch settles down on inclined tables, while the gluten passes on.

From this point, the hydrolysis proper begins.

The accumulated starch is transferred to closed copper or bronze converters, 6 ft. in diameter and 20 ft. high, in which a mixture is made of 100 parts of starch, 250 of water, and 0.5 per cent hydrochloric acid. The starch is introduced carefully and gradually and treated with steam at 30 lb. pressure. Hydrolysis takes place, to dextrins and glucose. For corn sirup, treatment for 30 min. is sufficient to accomplish the 40 to 50 per cent hydrolysis necessary, but, for corn sugar, fairly complete reaction is necessary, requiring 1 hr. 30 min. The mixture is then blown to neutralizing vats and exactly neutralized by sodium carbonate. This releases the remaining gluten, which is removed in filter presses, and he liquid is then passed through three filters, each 24 ft. high and 10 ft. in diameter and containing 35 tons of bone char. These remove the oloring matter, and the clear solution after evaporation *in vacuo* is rystallized for sugar production. The crystallization problem was not asy to solve, as glucose forms several varieties of both hydrated and nhydrous crystals. The bone char used in filtration is revivified and used.

Typical analyses of the two products are

Components	Corn sirup, %	Crystalline corn sugar, %
Water	19	4.0
Dextrose	38.5	94.6
Dextrin	42.0	0.7
Ash	0.5	0.7

The simple equation usually written to describe the hydrolysis of starch

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{HCl} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

gives a very inadequate conception of the process, which undoubtedly takes place in a number of stages.[1]

Saccharification of Wood. Hydrolysis with Dilute Sulfuric Acid

Scholler-Tornesch Process:

When cellulose is hydrolyzed according to the empirical equation

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H_2SO_4} nC_6H_{12}O_6$$

the resulting glucose, if left in contact with the acid at high temperature and pressure, is partly decomposed. The earlier plants built to hydrolyze wood used a batch cook in digesters under considerable steam pressure, much as the modern chemical pulp mills do, so that the glucose first formed was left in contact with the acid solution for some time. Hence, their final yield of glucose was the difference between the total produced by hydrolysis and the amount decomposed during the later stages of the cooking. Scholler has materially improved the yield by substituting pressure percolation for batch cooking, so that the resulting sugar is promptly removed and cooled before decomposition can set in. The commercial plant put in operation in 1930 at Tornesch (Holstein) is illustrated in Fig. 3.

The percolators are cylinders 31 ft. high with diameters from 5 to 6 ft. One is lead lined throughout, the others are protected by acidproof brick. The brick-lined percolators contain 5,000; the lead one, 6,150 gal. The lower ends of the cylinders are fitted with an acidproof filter, to separate the sugar-containing wort from the residues.

The small acidproof pump and the large water pump are used for the percolating liquid, and both are motor driven. The acid pump delivers sulfuric acid of 40 per cent strength from the reservoir. The water pump delivers water through the counterflow heater at a pressure of 10 atmos., the water being preheated by the inflowing hot wort. The water already warmed to about 150°C. is now heated to the reaction temperatures of 160 to 190°C. by means of fresh steam. The heated water reaches the mixing apparatus where 40 per cent sulfuric acid is added in such quantity that the material going to the percolator contains 0.2 to 0.6 per cent of acid. This mixture passes through the distributing pipe into the ring-shaped distributor and then flows through the percolators. After the hydrolyzing mixture has passed, either in series or in parallel as desired, through the contents of the percolators (always reaching the freshest wood last) and has absorbed the sugar formed, it enters the filter in the form of sugarwort and reaches the neutralizer. This neutralizer is filled with ordinary granulated phosphate and raw lime, thus neutralizing the sugarwort during its passage. The neutralized wort now enters the counterflow heater, heating the incoming cold fresh water. The cooled wort then passes the throttle valve and reaches the wort reservoir. The pressure used throughout is from 8 to 10 atmos.

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[1] An excellent bibliography of starch hydrolysis is given by R. P. Walton, "A Complete Survey of Starch Chemistry," Vol. I, Reinhold Publishing Corporation, New York, 1928.

The raw material at Tornesch consists of wood chips, sawdust shavings, machine shavings, and raspings. It need not be dry for this process nor must it all be finely divided or of uniform size. It is charged into the percolators through manholes, and the lignin residue is removed in the same way.

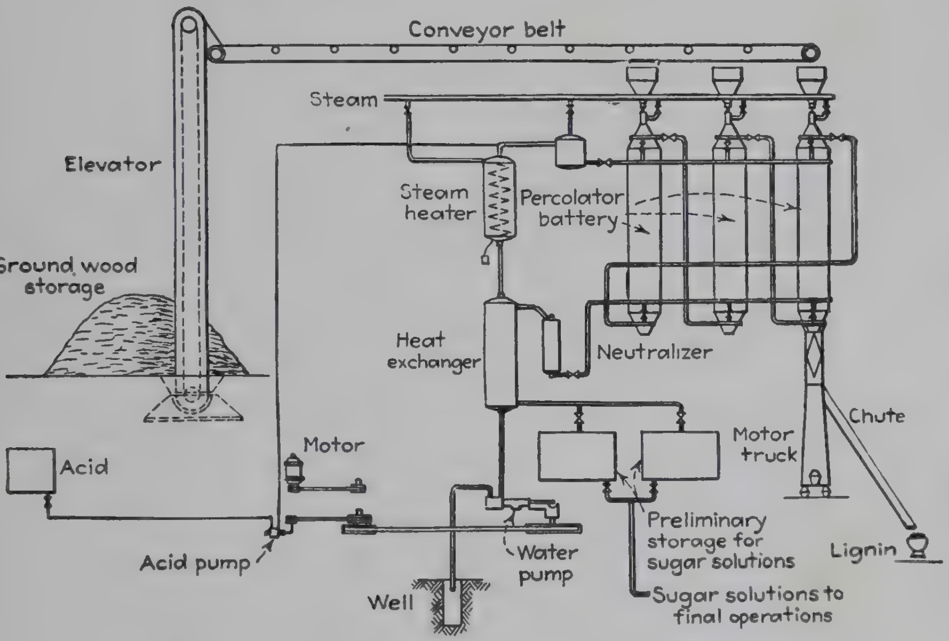
Conveyor belt
Steam
Elevator
Steam heater
Percolator battery
Ground wood storage
Heat exchanger
Neutralizer
Chute
Motor truck
Motor
Acid
Acid pump
Water pump
Preliminary storage for sugar solutions
Lignin
Well
Sugar solutions to final operations

FIG. 3.—Scholler-Tornesch system of wood saccharification.

Softwood material treated in this way yields about 40 gal. of 100 per cent alcohol per ton of dry wood by fermenting the crude sugar solutions. Even the bark of pine trees yields 25 gal. per ton. Based on a daily consumption of 60 tons of waste (dry) wood, the cost of a gallon of alcohol works out at 18 cts. per gallon, of which the wood itself based at $4.75 per ton accounts for 7.2 cts. So far, the only use to which the resulting lignin has been put is to supply the necessary heat for fermentation and distilling. It is very pure, has little ash, and briquettes easily. For a plant making alcohol by this process to pay its way requires that the by-product lignin be sold for more than approximately 1 ct. per pound. A process for producing crystallized glucose and zylose from the raw sugar has been developed.[1]

It will be observed that the essential feature of this scheme is the quick passage of acidulated water under pressure through the wood. To assure success, the temperature, concentration of acid, time of reaction, and rate of flow must all be well balanced.

Pilot-plant runs in a stationary digester using successive treatments of dilute H_2SO_4 have recently shown the following results.[2] Yields of total reducing sugars from softwoods, such as Douglas fir, spruce, and Southern yellow pine, ranged from 45 to 57 per cent of the weight of the wood; from hardwoods, such as oak and maple, 45 to 52 per cent; and from turpentine-spent chips, 35 to 37 per cent. The time for the hydrolysis and extraction, in several instances, was as low as 2.7 hr. Sugar concentrations greater than 6 per cent were obtained without loss in yield. The yield of alcohol per ton of wood ranged from 40 to 60 gal. from softwoods and from 33 to 42 gal. from hardwoods. A rotary digester was first used in determining the conditions required for hydrolysis and fermentation. Some of the results of this work are shown in the following table:

TABLE III.—HYDROLYSIS OF WOOD BY SUCCESSIVE TREATMENTS WITH DILUTE ACID IN A ROTARY DIGESTER

					Pressure, lb. per sq. in.		Yield	
Run No.	Species of wood	Dry wood, lb.	No. of cycles	Time of hydrolysis, hr.	Start	Final	Reducing sugar, %	Alcohol per ton dry wood, gal.
18	Spruce	28.9	8	2.0	125	190	40.0	41.0
19		29.6	9	2.2	125	190	33.7	40.0
26		42.7	10	2.5	50	180	39.0	41.0
27		44.0	11	2.7	65	180	44.0	47.5
28		44.0	11	2.7	112	180	41.0	44.3
29	Douglas fir	44.5	10	2.5	112	180	35.0	42.0

Use of Waste Sulfite Liquors.—As indicated above, some cellulose is hydrolyzed and sugars are formed during the process of treating wood chips by the sulfite process. The sugars in the waste sulfite liquor can be fermented to alcohol, and a process based on this raw material has been operated successfully from a technical viewpoint.[1] The waste liquor, containing 2.5 per cent reducing sugars and 1.8 per cent fermentable sugars, is desulfurized in a steam stripping column. The liquor is then screened to remove suspended pulp fibers and is cooled to 30°C. in a vacuum flash chamber. Lime slurry and urea are added by a proportioning device. Two continuous fermentation tanks in a series are used providing a total residence time of 20 hr. The effluent, containing 1 per cent yeast by volume, is separated in seven DeLaval continuous centrifuges, each with a capacity of 5,000 gal. per hr. The clarified liquid flows to a conventional still house. Recovery is 22 gal. of alcohol per ton of pulp, or 6,500 gal. per day. Operations in the plant are all continuous and automatic, and only three operators per shift are needed.

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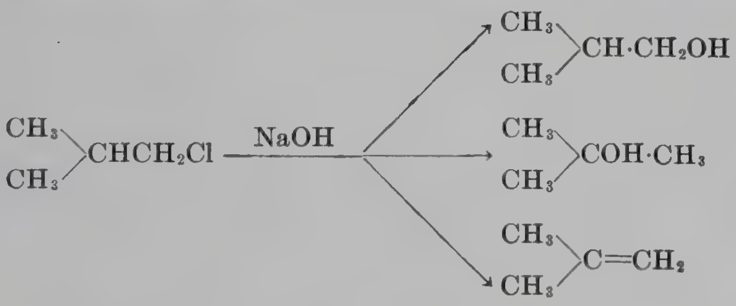
[1] BERGIUS, *Ind. Eng. Chem.*, **29**, 253 (1937).

[2] HARRIS, BELIGNER, HAJNY, and SHERRARD, *Ind. Eng. Chem.*, **37**, 12–23 (1945).

Hydrolysis of Butyl Chlorides. 1. *Conversion of Isobutyl Chloride.*



A mixture of 8 moles of isobutyl chloride, 8.4 moles of sodium hydroxide, and 205.5 moles of water is heated in a pressure vessel at 220°C. for a period of 10 min. On distillation, the reaction mass shows the presence of isobutyl alcohol 39.9 per cent; *tert*-butyl alcohol, 7.5 per cent; and isobutylene, 45.2 per cent. Data for similar experiments with various hydrolyzing agents are given in Table IV, page 698.[2]

A comparison of run 6 with runs 2, 10, and 11 shows that by employing a water-soluble metal hydroxide, *e.g.*, sodium hydroxide, as the hydrolyzing agent rather than a metal hydroxide which is relatively insoluble in water, *e.g.*, a hydroxide of calcium, lead, or magnesium, the yield of isobutyl alcohol becomes increased while the yields of *tert*-butyl alcohol and isobutylene are each lowered.

From a comparison of runs 8 and 9 with runs 2, 6, 10, and 11, it will be noted that by using an alkali metal carbonate or *bicarbonate* as the hydrolyzing agent, rather than a metal hydroxide under otherwise similar operating conditions, each of the alcohol products is formed in high yield and the yield of isobutylene is lowered.

The yield of *tert*-butyl alcohol can be increased at the expense of the

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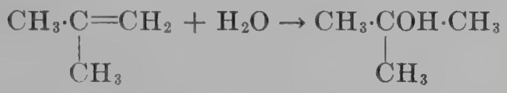
[1] Ericson, Puget Sound Pulp and Timber Company. Paper delivered at San Francisco Regional Meeting, *Am. Inst. Chem. Eng.*, August, 1946.

[2] U. S. 2,067,473 (1937).

TABLE IV.—HYDROLYSIS OF ISOBUTYL CHLORIDE

Run No.	Reaction mixture						Time of heating, hr.	Temperature, °C.	Conversion, %	Yield %		
	Isobutyl chloride, moles	Base		H_2O, moles	Mole ratio of H_2O to isobutyl chloride	Chemical equivalents of base per mole of isobutyl chloride				Isobutyl alcohol	*Tert*-Butyl alcohol	Isobutylene
		Kind	Moles									
1	6	$Ca(OH)_2$	3.24	66.7	11.1	1.08	4	185	96.5	19.0	8.6	66.4
2	4	$Ca(OH)_2$	2.16	88.8	22.2	1.08	4	170	95.2	21.8	21.7	53.3
3	2	$Ca(OH)_2$	1.08	88.8	44.2	1.08	4	165	98.1	21.7	27.0	45.5
4	4	$Ca(OH)_2$	2.10	205.5	51.4	1.05	0.25	220	97.5	23.6	26.6	43.7
5	6	NaOH	7.2	66.7	11.1	1.20	4	180	98.7	42.1	6.2	46.1
6	4	NaOH	4.32	88.8	22.2	1.08	4	155	91.5	43.2	9.1	41.4
7	4	NaOH	4.32	88.8	22.2	1.08	0.08	300	97.9	37.7	10.4	43.2
8	8	K_2CO_3	4.32	177.7	22.2	1.08	4	165	97.2	43.1	27.0	30.0
9	8	$NaHCO_3$	8.64	177.7	22.2	1.08	4	165	88.3	45.1	29.2	19.3
10	4	$Pb(OH)_2$	2.16	88.8	22.2	1.08	4	175	98.0	23.9	21.5	52.3
11	4	$Mg(OH)_2$	2.16	88.8	22.2	1.08	4	175	99.5	20.4	18.5	53.6

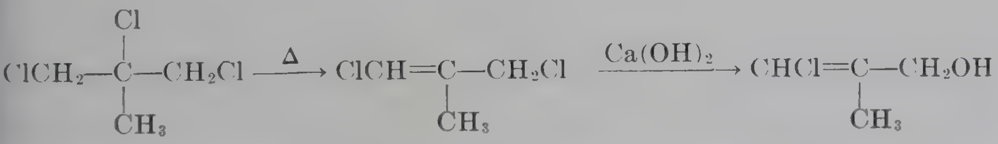
isobutylene by acidifying the hydrolyzed mixture with a strong acid, *e.g.*, sulfuric acid. If the operating procedure described above is repeated and the reaction mass acidified with H_2SO_4, so as to provide a 0.16 *N* aqueous sulfuric acid solution, and then heated under pressure, it is found that the isobutylene content is markedly reduced on fractionation and the products obtained are: isobutyl alcohol, 41.6 per cent; *tert*-butyl alcohol, 30.6 per cent; and isobutylene, 10.7 per cent. It is clear that two types of hydrolysis are here involved: (*a*) alkali hydrolysis and (*b*) catalytic acid hydration, *viz.*,



$$CH_3\cdot\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2 + H_2O \rightarrow CH_3\cdot\underset{\underset{\displaystyle CH_3}{|}}{C}OH\cdot CH_3$$

It is to be observed that addition of H·OH takes place according to Markownikoff's rule (see chapter on Halogenation).[1] As is to be expected, the sulfuric acid causes some polymerization of isobutylene to diisobutylene (2, 4, 4-trimethylpentene-1) to occur.

2. *Hydrolysis of* 1, 2, 3-*Trichloroisobutane.*—1, 2, 3-Trichloro-2-methylpropane may be converted to 3-chloro-2-methallyl alcohol by two methods. The first procedure occurs in two steps: (*a*) pyrolysis to effect dehydrochlorination to 1, 3-dichloroisobutene-1 and (*b*) hydrolysis of the chloroolefin.



$$ClCH_2{-}\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_2Cl \xrightarrow{\Delta} ClCH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CH_2Cl \xrightarrow{Ca(OH)_2} CHCl{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CH_2OH$$

In the second method, the trichloroisobutane is treated directly with alkali or alkaline-earth hydroxides to effect simultaneously the loss of hydrogen and tertiary chlorine as well as the replacement of one of the terminal chlorine atoms by a hydroxyl group. Here, only the second procedure will be described.[2]

Triisochlorobutane is delivered from its storage tank 2 (Fig. 4) to the digester 1 which contains approximately five volumes of milk of lime to one of the halogeno compound. If the hydrolyzer is maintained at a temperature of 180 to 220°C., a fairly complete conversion to 3-chloro-2-methallyl alcohol is obtained in about 1 hr. The reaction mass is delivered to the thickener 5, where the mixture separates into two layers, *viz.*, an upper layer containing water, calcium chloride, and alcohol with small quantities of trichlorobutane, and a lower layer containing the bulk of the unconverted halogeno compound, which is returned to the hydrolyzer along with calcium hydroxide, which collects for the most part at the bottom of the upper layer.

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[1] Markownikoff, *Ann.*, **153**, 256 (1876).

[2] U. S. 2,061,519 (1936).

The alcoholic layer is run off from the separator and delivered to an intermediate point in a continuous rectifying column 6, from the bottom of which a solution of calcium chloride, relatively free of chlorobutane, is withdrawn. The aqueous alcoholic vapors leaving the column are condensed and separated in a weir box 7 into reflux and take-off portions. The latter goes to the decanter 8 in which it separates into two layers: an upper layer consisting of water saturated with alcohol and trichlorobutane which is returned to the rectifier on a plate containing a liquid composition corresponding to the returned solution, and a lower layer consisting principally of alcohol saturated with water which is delivered to an intermediate point in the second rectifying column 6′ from the bottom of which a commercial grade of 3-chloro-2-methallyl alcohol (b.p., 163 to 164°C.) is withdrawn into the storage tank 10.

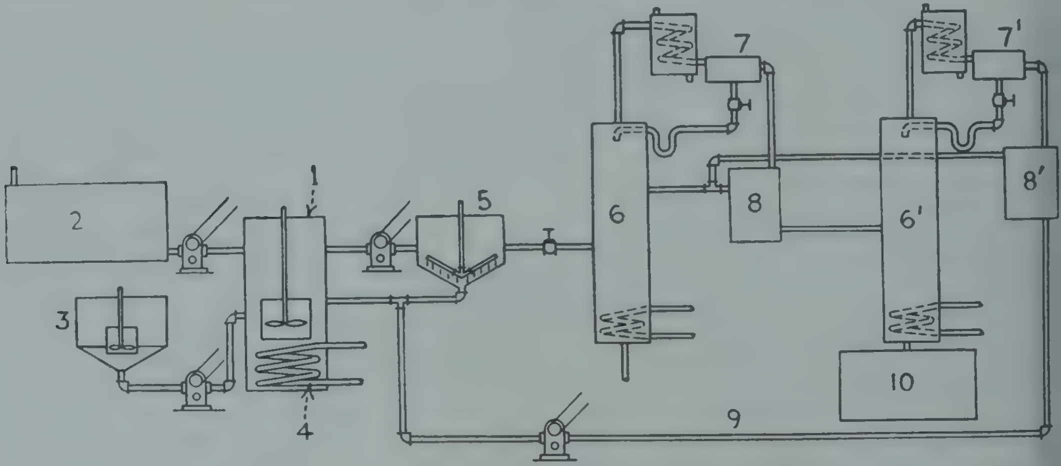

Fig. 4.—Flow diagram: hydrolysis of trichloroisobutane.

1. Digester or hydrolyzer.
2. Trichlorobutane holder.
3. Milk of lime slaking tank.
4. Heat-transfer coils for hydrolyzer.
5. Separator—thickener.

6-6′. Rectifying columns.
7-7′. Weir boxes.
8-8′. Decanters.
9. Return line to digester.
10. Alcohol storage.

The overhead product from the rectifier 6′ is condensed and separated for reflux and take-off as before. In the decanter 8′, the lower portion which contains some unreacted trichloroisobutane is returned to the digester.

Preparation of Amyl Alcohols from Chloropentanes.—New and enlarged uses for the amyl alcohols and their derivatives, particularly in pyroxylin lacquers, have called for enlarged production, which could not remain dependent upon incidental fusel oil from molasses and potato fermentation. This new production has come from the pentanes of natural gasoline through the chlorination-hydrolysis process developed by Ayres.[1]

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[1] Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929).

This process consists in the isolation from natural gasoline of two of the three pentanes; their chlorination (see chapter on Halogenation) to form monochlorides as far as possible; the hydrolysis under moderate pressure of these monochlorides by water containing sodium oleate and caustic soda; and, finally, the distillation of the alcohols from the reacting mixture. From the chlorination to the distillation inclusive, the process is continuous.

Hydrolysis is accomplished in a system of reservoirs, heaters, and pumps through which a hot emulsion of amyl alcohol, water, and sodium oleate is circulating at the rate of 500 gal. per min. Amyl chlorides and an aqueous solution of caustic soda are continuously pumped into this circulation material, and two things are continuously withdrawn: (1) a saturated salt solution, which is returned to electrolytic cells for manufacture of chlorine and caustic soda, and (2) a vapor containing principally amyl alcohols. Three hundred gallons of amyl chloride is present at all times in the hydrolysis system, and 300 gal. is hydrolyzed each hour.

The vapors from hydrolysis are separated by a train of fractionating columns into five components: (1) unchanged amyl chlorides, which are returned to hydrolysis; (2) amylene, which is later hydrated to amyl alcohol; (3) diamyl ether; (4) amyl alcohol fractions that are cut out for special uses; and (5) the mixture of amyl alcohols marketed under the trade name Pentasol for use in pyroxylin lacquers. The general layout is given in Fig. 5.

A condensed but inadequate description of the chlorination and hydrolysis is given by the equations

$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$
$$C_5H_{11}Cl + NaOH \rightarrow C_5H_{11}OH + NaCl$$

The operation of the hydrolysis can be followed from the accompanying diagram (Fig. 5). The mixture of water, caustic, sodium oleate, and amyl chloride is circulated through two digesters (only one is shown in the figure), one of which is larger than the other and serves also as a still. About 2 per cent of the amyl chloride present is hydrolyzed during each cycle. Like all other heterogeneous reactions, this proceeds more rapidly the more thoroughly the mixture is emulsified; and it has been found that, by introducing the caustic soda *before* the circulating pump, the agitation due to the latter much improves the emulsification. A temperature of 170°C. is maintained by a steam heater placed outside the digesters and through which the mixture is continually circulated.

Two pentanes (normal and iso) serve as starting products for chlorination, and these give rise to primary, secondary, and tertiary chlorides. The tertiary and secondary chlorides will hydrolyze with water; the primary and secondary, with sodium oleate. This catalyst really acts therefore in two ways: (1) It puts water in colloidal contact with amyl chloride, thereby promoting *rapid* hydrolysis of the secondary and tertiary chlorides; (2) it is itself in colloidal contact with the chlorides so that the primary and secondary compounds can form with it the amyl oleates, which are readily decomposed by caustic. Amyl chloride must not be present in excess over sodium oleate, or amylene will form in quantity.

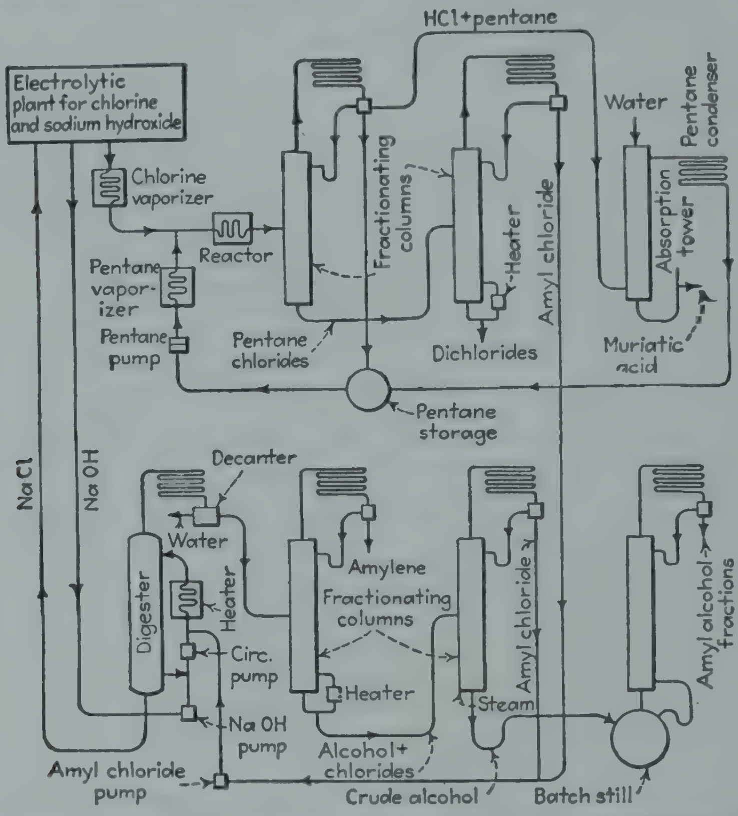
HCl+pentane
Electrolytic plant for chlorine and sodium hydroxide
Chlorine vaporizer
Reactor
Pentane vaporizer
Pentane pump
Fractionating columns
Pentane chlorides
Heater
Amyl chloride
Dichlorides
Water
Absorption tower
Pentane condenser
Muriatic acid
Pentane storage
NaCl
NaOH
Decanter
Water
Digester
Heater
Circ. pump
NaOH pump
Amyl chloride pump
Amylene
Fractionating columns
Heater
Alcohol+ chlorides
Amyl chloride
Steam
Crude alcohol
Batch still
Amyl alcohol fractions

FIG. 5.—Plant for production of amyl alcohols from pentane. (*According to E. E. Ayres.*)

The reaction is a surface one, and a coating of sodium oleate forms over the caustic, which must be mechanically dispersed; hence, the necessity for efficient agitation.[1]

Preparation of Alcohol from Olefins.—An abundant and hence cheap raw material is almost sure to find in time a use to which it can be economically put. The cracking of petroleum, especially vapor-phase cracking, produces tremendous volumes of olefin gases, which are now extensively used as raw materials for alcohol production. In addition, ethylene—the simplest of these—is present in small quantity in coke-oven gas. The alcohols made by this procedure are ethyl from ethylene, isopropyl from propylene, normal butyl indirectly from ethylene, secondary butyl from normal butylene, tertiary butyl from isobutylene, and secondary and tertiary amyl from amylenes. Attesting the economic importance of this process is the great number of recent patents granted in this field.

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[1] U. S. 1,953,745 (1934); AYRES, *Ind. Eng. Chem.*, **21**, 899 (1929); CLARK, *Chem. Met. Eng.*, **38**, 206 (1931).

All these alcohols are produced through reactions common apparently to all olefins—the union of the gas with concentrated sulfuric acid (or phosphoric acid) to form the corresponding monosulfate and the subsequent hydrolysis of this ester.

$$C_nH_{2n} + H_2SO_4 \rightarrow C_nH_{2n+1}OSO_3H \tag{1}$$

$$C_nH_{2n+1}OSO_3H + H_2O \rightarrow C_nH_{2n+1}OH + H_2SO_4 \tag{2}$$

It is interesting to note that the water molecule that enters the olefin distributes itself in such a way that the hydroxyl ion becomes attached to the carbon having the least hydrogen, so that secondary and tertiary alcohols—not primary—result.

The diluted acid must, of course, be reconcentrated for further use, which is a considerable item of cost. Apparently, the more complex the olefin the lower the temperature at which reaction (1) will take place. Ethylene requires a much higher temperature for efficient absorption than its homologues. Both mono- and dialkyl sulfates are formed simultaneously when ethylene or propylene is absorbed in sulfuric acid. An appreciable amount of diethyl sulfate is formed when the acid has reacted with about ⅓ mole of ethylene.[1] In addition, appreciable amounts of the corresponding ethers are produced. Ethyl ether, for example, is formed to a considerable extent by the reaction of alcohol with diethyl sulfate.[2]

$$(C_2H_5)_2SO_4 + C_2H_5OH \rightarrow (C_2H_5)_2O + C_2H_5HSO_4$$

Some recent processes use *dilute* acid under high pressures,[3] an increased yield of alcohol being obtained with a corresponding decreased yield of ether. The yield of ether may be also decreased by removal of alcohol from contact with unreacted sulfate liquor, as rapidly as it is formed, by immediate distillation in hot water.[4] Brooks and others have shown the advantages of absorption of ethylene under pressure.[5] Various catalysts are used in these processes,[6] and ethyl alcohol has been prepared by the direct combination of ethylene with water in the presence of catalysts and under pressure.[1]

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[1] Plant and Sidgwick, *J. Soc. Chem. Ind.*, **40,** 14T (1921).

[2] Brooks, *Ind. Eng. Chem.*, **27,** 283 (1935).

[3] U. S. 1,951,740; 1,955,417 (1934); 2,045,842; 2,050,442; 2,050,443; 2,050,444; 2,050,445 (1936).

[4] U. S. 2,038,512 (1936).

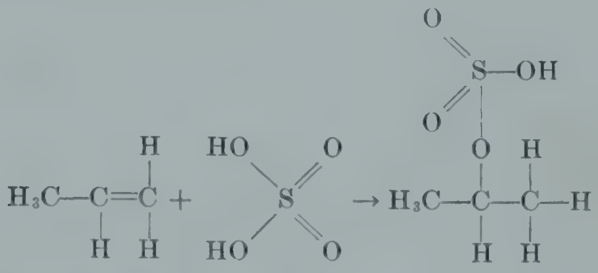
[5] Brooks, U. S. 1,885,585; 1,919,618 (1933); 1,960,633 (1934); *Ind. Eng. Chem.*, **31,** 518 (1939); Strahler and Hachtel, *Brennstoff-Chem.*, **15,** 166 (1934).

[6] U. S. 1,977,632 (1934); 1,999,620; 2,014,740 (1935); 2,051,046; 2,064,116 (1936); 2,087,290 (1937).

In the preparation of four carbon and higher alcohols, Schneider uses as catalysts, dilute solutions of sulfuric, phosphoric, or other acids, as well as metal halides.[2] Good yields of tertiary butyl alcohol are obtained by passing 11 per cent isobutylene through lead-lined absorption towers, 49 per cent sulfuric acid at 35°C. being used and 40 lb. per sq. in. pressure. According to Burk, acids that form volatile esters can be used to great advantage in the formation and handling of esters.[3] The ester is separated by distillation and subsequently hydrolyzed. Sulfuric acid, titanium chloride, boron fluoride, ammonium chloride, silver sulfate, mercury sulfate, etc., are effective catalysts.

In processes for olefin vapor-phase hydration, catalysts composed of one or more compounds of uranium, boron, copper, iron, manganese, cobalt, calcium, barium, strontium, magnesium, etc., show greater resistance to corrosion and greater mechanical stability.[4,5]

Preparation of Isopropyl Alcohol.—The particular olefin that will be absorbed by sulfuric acid free from catalysts is largely determined by the temperature and the concentration of the acid. Ethylene absorption takes place best between 93 and 120°C. (200 and 250°F.), whereas propylene is best absorbed between 21 and 27°C. (70 and 80°F.). At this last temperature, 97 per cent sulfuric acid will absorb approximately 50 per cent by weight of propylene. In commercial practice, the concentration of acid is even more significant than temperature for the formation of the specific alkyl sulfate. For example, the acid must be concentrated, *i.e.*, about 97 per cent for the formation of ethyl hydrogen sulfate, while propylene is absorbed in 85 per cent acid and the butene fraction in 75 to 80 per cent acid. However, dilute acid can be used at high temperatures and pressures.[6]



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[1] U. S. 1,977,632; 1,978,266; 1,978,270 (1934); 2,084,390 (1937); Bliss, *Ind. Eng. Chem.* **29,** 19 (1937).

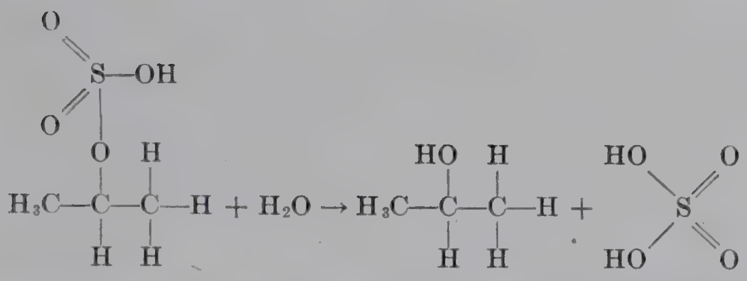
[2] Schneider, U. S. 2,221,955 (1940).

[3] Burk, U. S. 2,317,949 (1943).

[4] U. S. 2,292,561 (1942).

[5] U. S. 2,232,610 (1941).

[6] Brooks, *Ind. Eng. Chem.*, **31,** 518 (1939).



$$H_3C-CH(OSO_2OH)-CH_2-H + H_2O \rightarrow H_3C-CH(OH)-CH_2-H + (HO)_2SO_2$$

The cracking still gases, after losing their gasoline constituents by compression or absorption, are passed through fuller's earth impregnated with calcined copper oxide, which takes out completely the sulfur compounds (see Fig. 6[1]). The absorption of the propylene is accomplished by passing the gases through an absorption tower cooled by brine to hold the temperature between 24 and 27°C. (75 and 80°F.). The reaction is strongly exothermic.

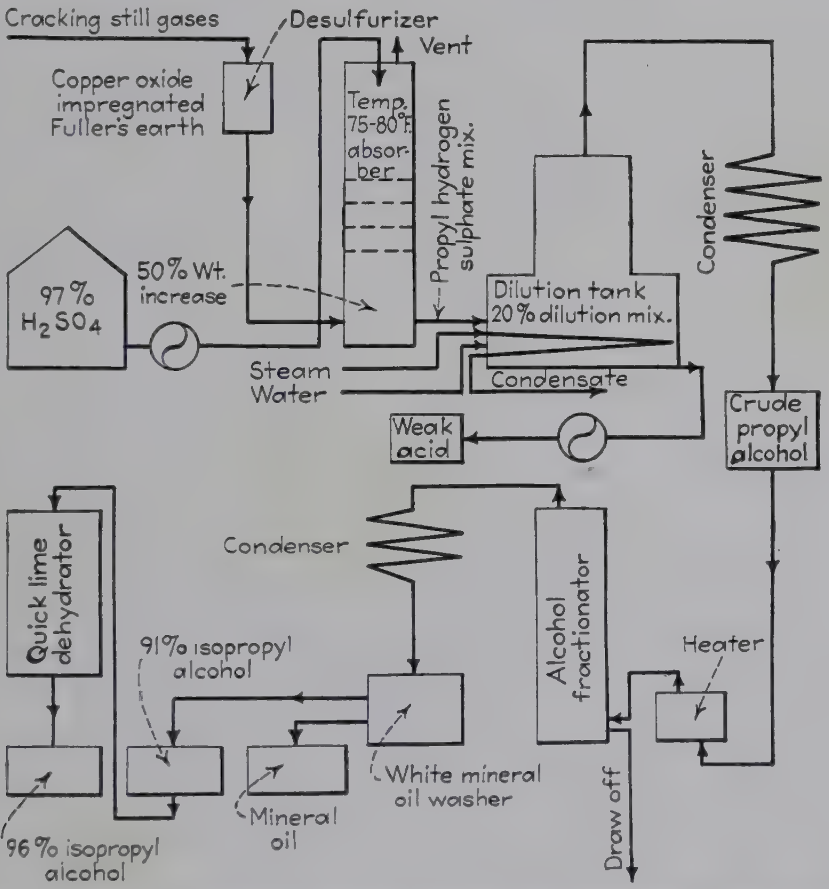

Cracking still gases
Desulfurizer
Vent
Copper oxide impregnated Fuller's earth
Temp. 75-80°F. absorber
Propyl hydrogen sulphate mix.
Condenser
97% H_2SO_4
50% Wt. increase
Dilution tank 20% dilution mix.
Steam
Water
Condensate
Weak acid
Crude propyl alcohol
Quick lime dehydrator
Condenser
Alcohol fractionator
Heater
91% isopropyl alcohol
White mineral oil washer
Draw off
Mineral oil
96% isopropyl alcohol

Fig. 6.—Plant for the production of isopropyl alcohol from propylene in cracking still gases.

Practically no ethylene is absorbed at this temperature, but the higher olefins, such as butylene, amylene, and hexylene, are absorbed along with propylene. In some plants, batch absorbers equipped with cooling coils and high-speed agitators are used. The reaction mixture is drawn from the absorber to lead-lined equipment and diluted with two or three volumes of water or steam. The heat of dilution warms up the mixture, and additional steam is used to drive off the dilute crude alcohol. This is then sent to the rectifier for concentration, and a 91 per cent technical isopropyl alcohol is obtained. Chlorine, sodium hypochlorite, or potassium permanganate is used for purification.

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[1] From *Refiner and Natural Gasoline Mfr.*, 225, February, 1932.

The higher alcohols are much more soluble in white mineral oil than is isopropyl and are removed by selective absorption. Absolute iso-

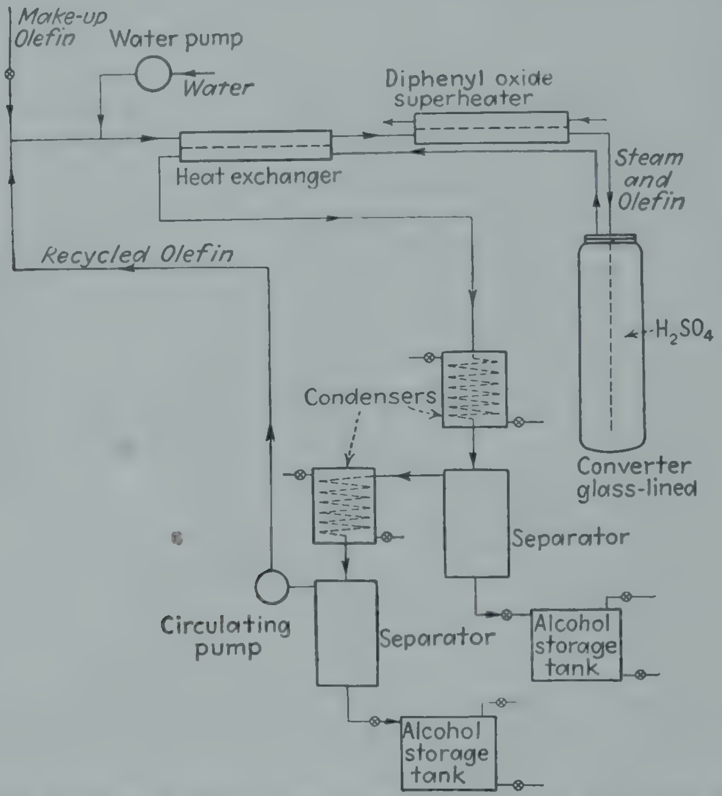
Make-up Olefin
Water pump
Water
Diphenyl oxide superheater
Heat exchanger
Steam and Olefin
Recycled Olefin
H_2SO_4
Condensers
Converter glass-lined
Separator
Circulating pump
Separator
Alcohol storage tank
Alcohol storage tank

FIG. 7.—Flow diagram: continuous vapor-phase production of alcohols from olefins.

propyl alcohol—which constitutes most of commercial production—may be made by using benzene for the azeotropic removal of water from 91 per cent material. The diluted sulfuric acid (sp. gr., about 1.4), is concentrated to specific gravity 1.8 and returned to the absorption step, but the gradual accumulation of polymerized and tarry material in the acid makes it necessary to discard it ultimately. A yield of 85 per cent of propylene in the gases is obtained in the form of isopropyl alcohol.

Continuous Vapor-phase Production of Alcohols from Olefins.—The continuous preparation of alcohols from olefins can be carried out in the apparatus shown diagrammatically in Fig. 7.[1] For the preparation of ethanol, fresh and recycled ethylene are mixed with water and passed under pressure through a heat exchanger and then through a superheater kept at approximately 300°C. The heated reactants as vapors are delivered under a pressure of about 900 lb. per sq. in. into a converter containing dilute (*i.e.*, $<$ 50 per cent) sulfuric or phosphoric acids. Because the temperature of the acid is above its normal boiling point, it acts as a catalyst to convert part of the ethylene and steam to ethanol. The alcohol admixed with unreacted vapors is passed through a series of condensers and separators. The condensed aqueous ethanol is collected for rectification, and the uncondensed ethylene is recycled under pressure.

---

[1] U. S. 2,087,290 (1937).

The proportions of steam and olefin will vary depending on the temperature, pressure, and acid concentration, these factors being interdependent. The pressure converter is made of steel, lined with lead. To protect the lead lining against the dilute acid at high temperatures, an inner insulating lining of glass bricks is used. Proper dispersion of the reacting vapors through the superheated mineral acid is obtained by providing the pressure converter with a distributer and using Raschig rings as packing.

Preparation of Ethylene Glycol.

$$CH_2OHCH_2Cl + NaHCO_3 \rightarrow CH_2OHCH_2OH + NaCl + CO_2$$

The chlorohydrin for this process may be made as follows:[1] Ethylene gas in fine bubbles is passed through a cooled hypochlorous acid solution in a reaction tower, the ethylene being in excess at all times and the temperature remaining below 10°C. The solution passes through a second cell, where more chlorine is added to transform the residual sodium hypochlorite to hypochlorous acid, and ethylene again passed through in a reaction tower. Chlorites and hypochlorites are removed by sodium bisulfite, and the solution made neutral by calcium carbonate. Solutions containing 20 per cent ethylene chlorohydrin can be made in this way and may be concentrated to 35 to 40 per cent by distillation. The chlorohydrin solution is now ready for hydrolysis and is treated with the exact amount of sodium bicarbonate solution required at a temperature of 70 to 80°C. with constant stirring. The reaction is carried out in a closed steam-jacketed kettle provided with a stirrer, and the carbon dioxide evolved is used to carbonate fresh caustic solution. Hydrolysis proceeds smoothly with a continuous evolution of carbon dioxide and under normal conditions is completed in 4 to 6 hr. The glycol solution may be concentrated in a steam-jacketed vessel and under reduced pressure if desired.

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[1] See also chapter on Halogenation.

Ethylene glycol may be prepared by reacting ethylene dichloride with alkalies or alkaline-earth carbonates or bicarbonates and boiling in an autoclave under pressure at approximately 150 to 170°C.[1] It may also be prepared from ethylene, oxygen, and water in the presence of catalysts.[2] The primary action is the formation of ethylene oxide,[3] which then readily adds water to form the glycol

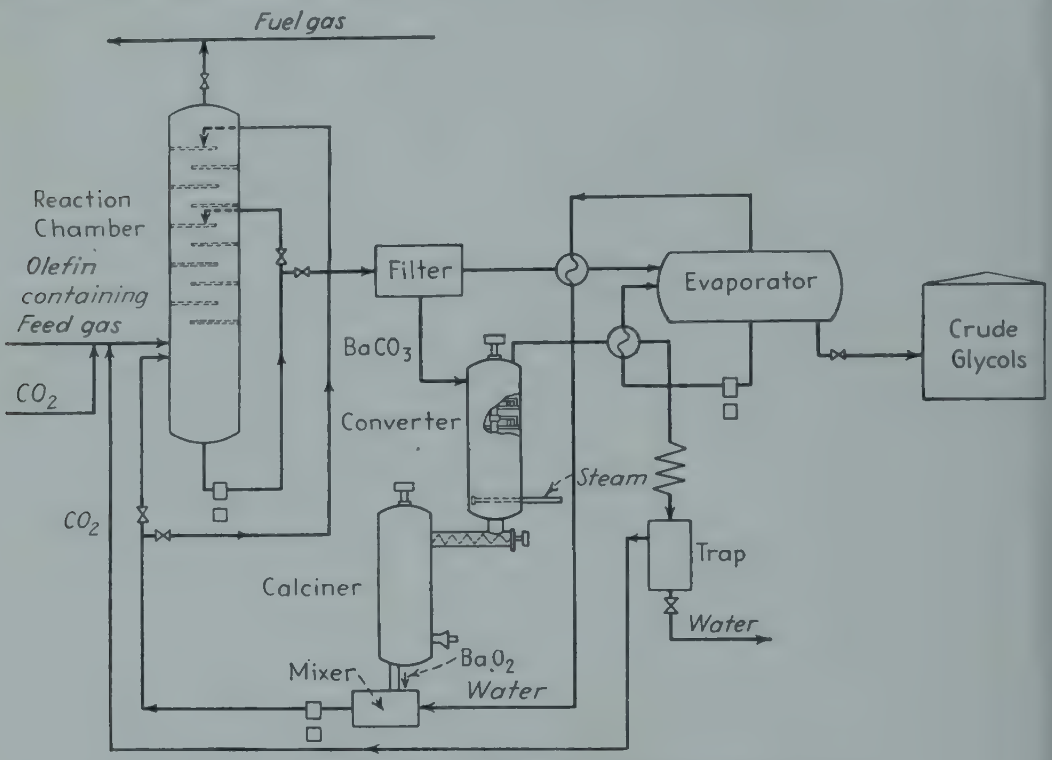
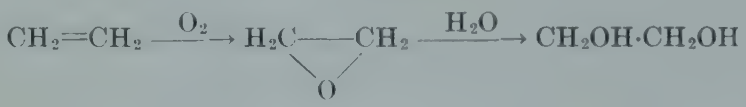

Fuel gas
Reaction Chamber
Olefin containing Feed gas
CO_2
CO_2
Filter
$BaCO_3$
Converter
Evaporator
Crude Glycols
Steam
Trap
Water
Calciner
Mixer
BaO_2
Water

FIG. 8.—Flow diagram: production of glycols from olefins.



$$CH_2{=}CH_2 \xrightarrow{O_2} H_2C\text{—}CH_2\,(\text{—O—}) \xrightarrow{H_2O} CH_2OH{\cdot}CH_2OH$$

Finally, glycols may be made by mixing olefin gases with carbon dioxide and contacting with a solution of barium peroxide.[4] The process is illustrated diagramatically in Fig. 8. Unsaturated gases are introduced, along with carbon dioxide, into the reaction chamber and conducted upward where they are contacted by means of suitable baffles with a down flowing aqueous suspension and partial solution of barium peroxide. The following reaction, using ethylene, takes place:

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[1] U. S. 1,695,250 (1928); U. S. 1,928,240 (1933); Fr. 774,186 (1934); U. S. 2,041,272 (1936).

[2] Fr. 722,000 (1931); Ger. 561,049 (1930); 619,195 (1935); U. S. 1,982,545 (1934); 2,071,395 (1937).

[3] U. S. 1,998,878 (1935) also Reissue 20,370 (1937).

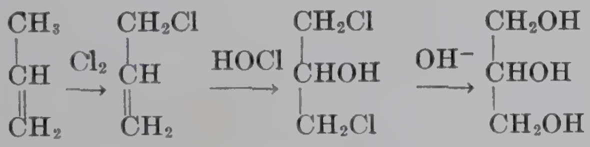
[4] U. S. 2,249,986 (1941); 2,367,324 (1945).

$$BaO_2 + CO_2 + C_2H_4 + H_2O \rightarrow C_2H_4(OH)_2 + BaCO_3$$

The converter is an insulated chamber equipped with trays and agitators for drying the barium carbonate and subjecting it to a high temperature. By the use of superheated steam, barium carbonate is converted into barium oxide, and this is withdrawn to the calciner for the regeneration of barium peroxide.

Mixed glycols which are suitable as antifreeze agents can be made from ethylene and propylene. The cracking-still mixture is treated in an absorption tower with chlorine in the presence of water to produce a 15 per cent chlorohydrin solution. In a separate still, the chlorohydrins are separated from alkalene chloride and hydrochloric acid as a constant-boiling mixture (b.p., 96°C.) by distillation with steam. These are converted to alkalene oxides by treatment with hydrated lime. The oxides are further hydrolyzed by 0.5 per cent sulfuric acid to glycols. The sulfuric acid is precipitated by the addition of lime and removed as calcium sulfate. The mixture of crude glycols is then purified by distillation.[1]

Preparation of Glycerol.—When propylene is chlorinated at temperatures above 200°, yields of 85 to 90 per cent of allyl chloride are obtained.[2,3,4] This can be converted to glycerol by a number of procedures, one of which is depicted below.[5,6]



$$\begin{array}{c}CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} \xrightarrow{Cl_2} \begin{array}{c}CH_2Cl\\ |\\ CH\\ \|\\ CH_2\end{array} \xrightarrow{HOCl} \begin{array}{c}CH_2Cl\\ |\\ CHOH\\ |\\ CH_2Cl\end{array} \xrightarrow{OH^-} \begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

Allyl chloride derived by the vapor phase chlorination of propylene is converted to a mixture of glycerol dichlorohydrins by chlorohydrination. High yields of glycerol are obtained by the subsequent hydrolysis of the dichlorohydrins.

Hydrolysis of glycerol dichlorohydrin presents roughly the same problems as that of the monochlorohydrin. It is possible to convert glycerol dichlorohydrin to epichlorohydrin by treatment with lime, with subsequent conversion to the monochlorohydrin and then to glycerol. Full investigation on a pilot-plant scale has shown that once allyl chloride is obtained, the preferred routes to glycerol are either hydrolysis to allyl alcohol,[1] followed by chlorohydrination and hydrolysis, or direct chlorohydrination[2] of the allyl chloride with subsequent hydrolysis.

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[1] U. S. 2,103,849 (1937).

[2] U. S. 2,077,382 (1937); 2,062,002 (1936); 2,130,084 (1938); Groll, Hearne, Rust, and Vaughan, *Ind. Eng. Chem.*, **31**, 1239–1244 (1939).

[3] U. S. 2,070,990 (1937); 2,086,077 (1937).

[4] U. S. 2,321,037 (1943).

[5] Brooks, *Ind. Eng. Chem.*, **31**, 515–519 (1939); Williams, *Trans. Am. Inst. Chem. Eng.*, **37**, 157–207 (1941).

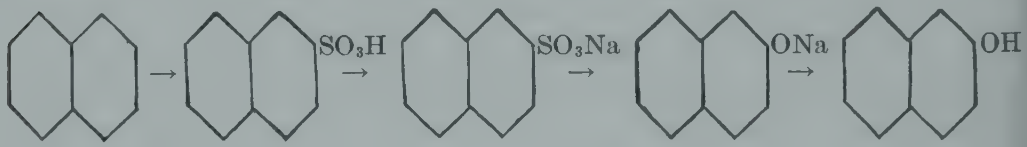
[6] Williams, *Trans. Am. Inst. Chem. Eng.*, **37**, 189 (1941); Fairbairn *et al.*, *Chem. Eng. Prog.*, No. 6, 280–290 (1947).

A 90 per cent yield of 1, 2, 3-trichloropropane[3] may be obtained by chlorination of propylene dichloride in the presence of an iron catalyst and ultraviolet light. This yields glycerol upon hydrolysis.

Production of β-Naphthol.—Fusion with sodium or potassium hydroxide has been found useful in introducing the hydroxyl radical into aromatic nuclei that have previously been sulfonated or halogenated, the alkali metal combining with the sulfonic group or halogen atom and substituting its own hydroxyl. The older commercial method for synthesizing phenol involves sulfonation of benzene and subsequent caustic fusion. Similarly, carvacrol and alizarin are made by sulfonating cymene and anthraquinone, respectively, and fusing the resulting sodium sulfonates with caustic. The production of β-naphthol, an important intermediate, will be described as an example of this type of hydrolysis.

β-Naphthol is made from naphthalene by sulfonating it, then desulfonating with steam the small proportion (15 per cent) of the alpha acid formed, converting the free β-sulfonic acid to the sodium salt with sodium chloride, fusing the sodium naphthalenesulfonate with caustic to form sodium β-naphtholate, and releasing the free naphthol by acid.

The sulfonation process is discussed in a separate chapter, and only those steps following the production of the sodium naphthalenesulfonate will be dealt with here. The complete chain of reactions is as follows:[4]



To convert the sodium naphthalenesulfonate into the sodium naphtholate, the following procedure may be adopted. Caustic soda is introduced into the fusion pot—a deep vessel 7 ft. 3 in. in diameter—water is added, and the mixture is stirred and heated until the temperature reaches 305°C. At this point, the sodium naphthalenesulfonate, containing 30 per cent water, is added until the temperature drops to 295°C.; the temperature is then allowed to rise; and more sulfonate added until all has been introduced. The temperature is kept always between 295 and 305°C. during the introduction of the sulfonate. The fusion is now maintained for 6 hr. at 300°C., after which it is discharged into the weak wash waters obtained by the treatment of a previous batch. For this step, the relative weights of materials are

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[1] U. S. 2,313,767 (1943).

[2] U. S. 2,296,687 (1942).

[3] U. S. 2,119,484 (1938).

[4] Shreve, *Color Trade J. Textile Chem.*, **14**, 42 (1924).

Sodium naphthalenesulfonate	21.8
95% caustic soda	6.6
Water	1.0

The weak washings just mentioned are contained in quenching tanks, each having a capacity of 3,500 gal., in which the fused mass from the previous step dissolves more or less completely. The resulting hot solution is filtered through iron filter presses, the filtrate going into the acidification tanks, while the washed cake is discarded. To convert the sodium salt of the β-naphthol into the naphthol itself, the following procedure may be used:

Into the hot filtered solution, dilute sulfuric acid is run until the mixture is acid to phenolphthalein. If necessary, live steam is turned in to raise the temperature to 200°F. (93°C.), thereby liquefying the β-naphthol. After 20 min. standing, a separation will have taken place, the sulfite liquor lying at the bottom with the crude β-naphthol floating on top. The sulfite liquor is then run into a separate tank, where it is cooled to recover the 10 per cent of naphthol contained in it. The liquid naphthol is then transferred to the wash tank and washed repeatedly and thoroughly until the wash water shows a specific gravity of 1. The crude naphthol is then dried with steam at 115°C. and transferred to the still. Here a temperature of 200°C. is maintained at first, without vacuum, but the main distillation is carried out with 28 in. of vacuum and at 248°C. The naphthol distills over into cooled zinc-lined boxes, where it solidifies. The necessary fine powdering is effected by a Raymond mill.

A 74 per cent yield is obtained from the caustic fusion point to final salable product, and a 64 per cent yield based on the naphthalene used.

For a plant capable of producing 8,000 lb. of β-naphthol by the above complete process, the raw-material list is

	Pounds
Naphthalene	11,200
Sulfuric acid (93%)	13,370
Sulfuric acid (50%)	10,200
Salt	20,000
Caustic soda (95%)	7,900
Abundance of water	
Total	62,670

It will be seen that the weight of the raw materials is nearly eight times that of the final product. By a proper integration of operating steps, this ratio can be substantially reduced; in the manufacture of phenol, about 4.3 lb. raw material per pound of product is required.

Manufacture of Synthetic Phenol.—Synthetic phenol from benzene affords examples of three commercial methods of manufacture by hydrolysis. The process that dominated the field at first involves the caustic fusion of sodium benzenesulfonate. In this process, a seemingly large number of separate operations are required to effect the simple transformation

$$C_6H_6 \rightarrow C_6H_5OH$$

Although the by-products in each step of this process are advantageously employed in some phase of the synthesis, it is obvious, from the description below, that relatively large quantities of materials (4.3 lb. per lb. phenol) have to be handled. The process of the Dow Company, which now accounts for a substantial percentage of domestic production, starts from chlorobenzene, hydrolyzing it under high pressure in an aqueous alkaline solution with copper as catalyst.

Patents[1] by Raschig and his associates describe processes whereby chlorobenzene is prepared from benzene by use of hydrochloric acid and oxygen at temperatures above 150°C., the chlorobenzene then being hydrolyzed by steam at temperatures above 350°C. The phenol and hydrochloric acid formed are separated from the reaction products while they are still in the gaseous state.

$$C_6H_6 + HCl + O \rightarrow C_6H_5Cl + H_2O$$
$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$$

Sulfonation and halogenation of benzene are described in other chapters of this book. The initial discussion of phenol production will start with sodium benzenesulfonate and chlorobenzene as raw materials.

Phenol from Benzenesulfonic Acid.—The reaction involved in the caustic fusion of sodium benzenesulfonate to form sodium phenoxide is

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

A typical mode of operation is as follows:

About 2,000 lb. of fused caustic soda is put into the fusion kettle immediately after a previous run has been discharged. The lumps are permitted to melt for about 1 hr., and 40 to 50 gal. of water is added. The heating (with gas or oil) is started, and the temperature brought up to 280°C. in a period of 1 hr. The temperature will continue to rise to 300 to 320°C., at which time the solution of sodium benzenesulfonate is pumped, in a regulated manner, *under* the surface of the caustic melt. About three molecular equivalents of alkali are employed. Since exposure to air appreciably diminishes the yield of phenol, it is necessary to have a submerged feed for the sulfonate.

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[1] Raschig, Fr. 730,462 (1932); 756,814 (1933); Ger. 588,649 (1933); U. S. 2,009,023 (1935); 2,035,917 (1936).

The temperature is maintained at 305 to 310°C. for 6 hr. and brought up to 330°C. for an hour before the run is completed. The temperatures are about the same as those used in the fusion for β-naphthol production. Since the sodium sulfite formed is practically insoluble in a concentrated solution of caustic soda containing sodium phenoxide, the fusion mass is run into a vessel containing a measured quantity of sodium phenoxide wash waters from previous charges. The sodium sulfite separates out and is filtered off by pumping the aqueous suspension onto a nickel gauze or into a centrifugal filter. A saturated solution of sodium sulfite[1] or organic solvents[2] may be used to extract the sodium phenoxide from the sodium sulfite.

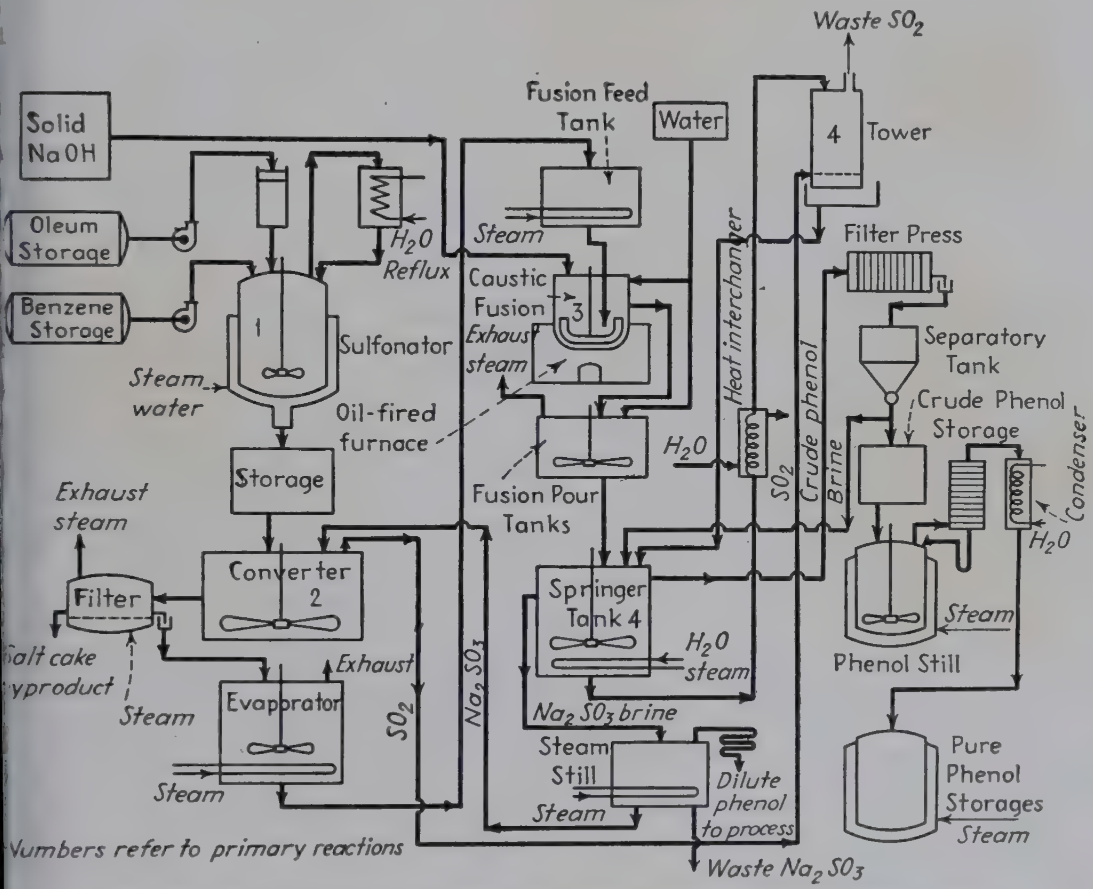
Waste SO_2
Fusion Feed Tank
Water
4
Tower
Solid NaOH
Oleum Storage
Benzene Storage
H_2O Reflux
Steam
Caustic Fusion
3
Exhaust steam
Filter Press
1
Sulfonator
Heat interchanger
Separatory Tank
Crude Phenol Storage
Steam water
Oil-fired furnace
H_2O
Crude phenol
SO_2
Brine
Condenser
H_2O
Storage
Exhaust steam
Fusion Pour Tanks
Converter 2
Filter
Springer Tank 4
Steam
Phenol Still
alt cake
yproduct
Exhaust
H_2O steam
Steam
Evaporator
SO_2
Na_2SO_3
Na_2SO_3 brine
Steam Still
Dilute phenol to process
Pure Phenol Storages
Steam
Steam
Steam
umbers refer to primary reactions
Waste Na_2SO_3

FIG. 9.—Flow diagram: production of phenol *via* sodium benzenesulfonate.

The water from previous washes is taken for the first wash, and this added to the solution of sodium phenoxide. The next two washes are saved for use in the quenchers and for washes, respectively.

Neutralization of the sodium phenoxide to release the phenol may be done by carbon dioxide, mineral acids, benzenesulfonic acid, or preferably with the SO_2 liberated when the benzenesulfonic acid is treated with the by-product Na_2SO_3 to form the required sodium benzenesulfonate. Usually, some sulfuric acid must be finally added to ensure complete neutralization. The phenol containing some water separates out as an upper layer over an aqueous solution containing the appropriate sodium salt. The phenolic layer is separated and distilled *in vacuo*, while the aqueous layer, which still contains some phenol, goes back to the operating cycle.

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[1] U. S. 2,334,488 (1943).

[2] U. S. 2,281,485 (1942).

A simplified flow sheet of operations is given in Fig. 9.[1] The primary chemical reactions are as follows:

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O \tag{1}$$

$$2C_6H_5SO_3H + Na_2SO_3 \rightarrow 2C_6H_5SO_3Na + H_2SO_3 \tag{2}$$

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O \tag{3}$$

$$2C_6H_5ONa + H_2SO_3 \rightarrow 2C_6H_5OH + Na_2SO_3 \tag{4}$$

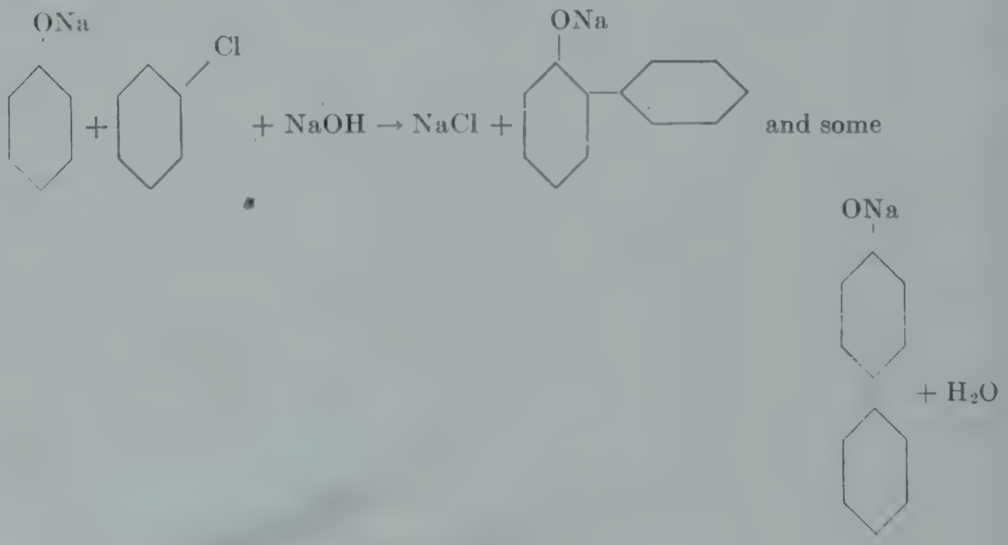
Phenol from Chlorobenzene, Dow Process.—The Dow phenol process is based on the hydrolysis of chlorobenzene in caustic soda solution at temperatures of about 360° and pressures of about 4,000 lb. per sq. in. Although the basic reaction was discovered in 1914 by Meyer and Bergius,[2] the development of the commercial application of the reaction had to await the introduction of satisfactory materials of construction and the solution of a number of chemical and chemical engineering problems.

The fundamental reactions are as follows:

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O \tag{1}$$

$$C_6H_5ONa + C_6H_5Cl \rightarrow C_6H_5—O—C_6H_5 + NaCl \tag{2}$$

Side reactions also occur as follows:



(3)

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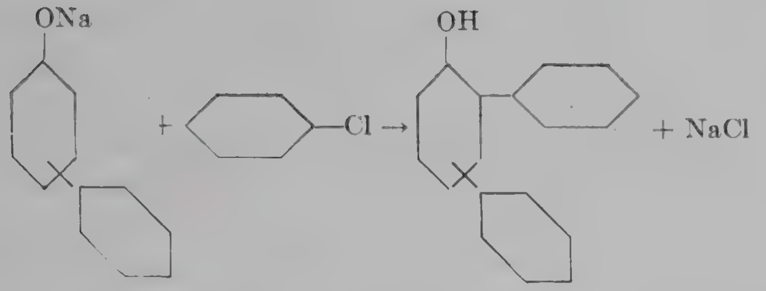
[1] Callaham, *Chem. Met.*, **49**, 76 (1942).

[2] Meyer and Bergius, *Ber.*, **47**, 3155 (1914).



(4)

Aylsworth showed that the reaction could be carried out by pumping the reaction mixture at elevated temperatures through a tubular pressure system.[1] Putnam found that, by the use of heat exchange, the heat requirements of the reaction could be supplied by the exothermal reaction, thereby providing an economic basis of operation.[2] Finally, Hale and Britton showed that the diphenyl ether [Eq. (2)] produced in the process could be returned as a reaction ingredient, thereby maintaining a constant relationship in the output of phenol and ether.[3]

The plant for carrying out the process consists of a mixing tank for thoroughly mixing chlorobenzene, diphenyl ether, and caustic soda solution; a hydraulic pump capable of producing pressures up to 10,000 lb. per sq. in.; a tubular autoclave, preferably built-in heat-exchange design, containing about 4,500 lineal feet of 1½-ft. XX heavy pipe; a cooling coil; an accumulator-actuated discharge valve;[4] and the necessary storage tanks for the several products.

The reaction is carried out by placing in the mixing tank a mixture containing 2 ¼ moles of caustic soda as a 10 per cent solution per mole of chlorobenzene. After a good mixture has been obtained, the hydraulic pump is started and the mixture is initially heated to 350°C., which starts the reaction. With continuous pumping being carried on, the mixture enters the heat-exchange path; and after this equipment has been warmed up, the preliminary heating may be virtually eliminated because the reaction is thence continued in heat-exchange relation. The pumping rate is such that the mixture traverses the tubular autoclave in about 20 min. The pressure will be about 4,500 lb. per sq. in., although the vapor pressure of the solution would be only about 3,000 lb. per sq. in., the extra pressure being due to the pipe system itself. The accumulator discharge is set at about 3,200 lb. per sq. in. After many days of operation, the pressure necessary to force solution through the tubular autoclave increases owing to the formation of Fe_3O_4 in the tubes with subsequent partial plugging. This proceeds to a point where the system

[1] Aylsworth, U. S. 1,213,143 (1917).

[2] Putnam, U. S. 1,921,373 (1933).

[3] HALE and BRITTON, *Ind. Eng. Chem.*, **20**, 114 (1928).

[4] Griswold, U. S. 1,602,766 (1926).

is completely plugged. The tubular autoclave is then dismantled, cleaned out, and repaired if necessary, and the cycle is resumed.

After the phenoxide solution is discharged from the autoclave, it is extracted with chlorobenzene to remove all alkali-insoluble material, *viz.*, diphenyl ether and phenyl xenyl ether. The reaction mass is then acidified with hydrochloric acid to neutralize excess caustic and to liberate the phenols. The aqueous layer is put through a steaming-out tower to recover all dissolved phenol. The phenol layer is distilled to recover phenol, following which distillation is continued to recover ortho and para phenylphenols which are further purified for sale.

In the process, the chlorobenzene is converted to about 78 per cent phenol, 11 to 12 per cent diphenyl ether, 7 to 8 per cent phenylphenols, 2 to 3 per cent higher ethers, and by-product tars and phenols. When the diphenyl ether is returned to the system as produced, the amount of chlorobenzene added is lessened by its diphenyl ether equivalent, and approximately the same amount of products are produced.

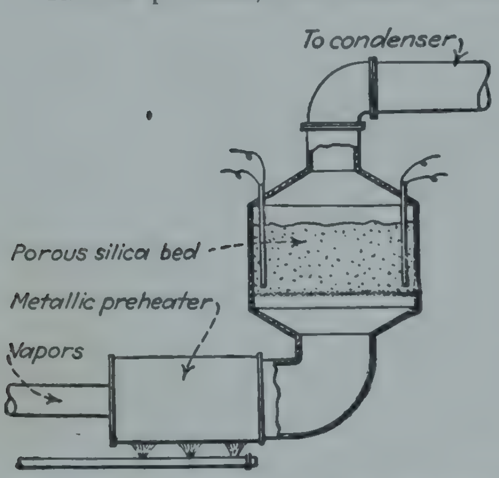

To condenser
Porous silica bed
Metallic preheater
Vapors

Fig. 10.—Apparatus for vapor-phase hydrolysis of chlorobenzene with steam.

Vapor-phase Hydrolysis of Chlorobenzene.—The direct production of phenol by the interaction of steam and chlorobenzene, with hydrochloric acid as a by-product, has naturally attracted attention and has resulted in a few patents.[1] In pilot-plant operation, a yield of over 90

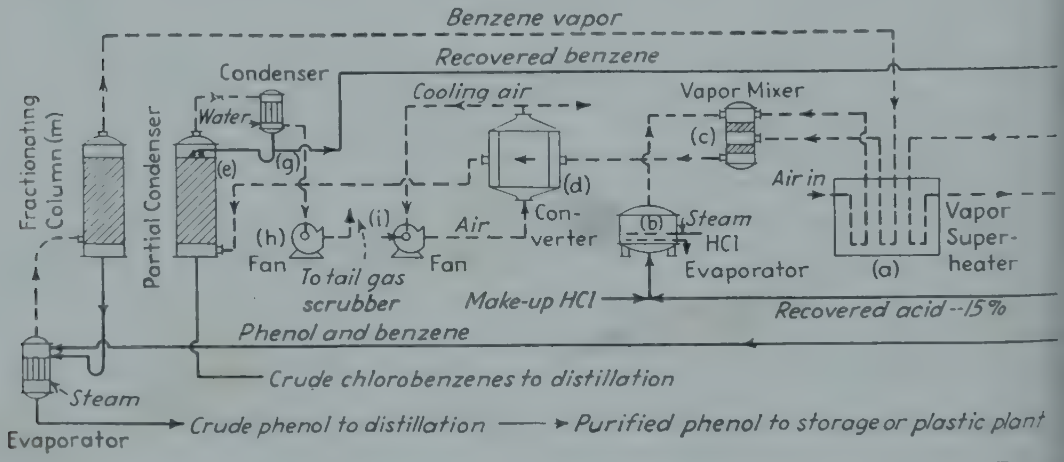

Benzene vapor
Recovered benzene
Condenser
Water
Cooling air
Vapor Mixer
Fractionating Column (m)
Partial Condenser
(e)
(g)
(c)
(d)
Air in
(h)
Fan
(i)
Fan
Air
Con-verter
(b)
Steam
HCl
Evaporator
Vapor Super-heater
(a)
To tail gas scrubber
Make-up HCl
Recovered acid--15%
Phenol and benzene
Crude chlorobenzenes to distillation
Steam
Evaporator
Crude phenol to distillation
Purified phenol to storage or plastic plant

Fig. 11.—Durez

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[1] U. S. 1,735,327 (1929); 1,849,844; 1,884,710 (1932); 1,936,567 (1933); 1,950,359; 1,961,834; 1,966,281 (1934); Brit. 288,308 (1929); 354,948; 358,903 (1931); Jap. 91,160 (1931); Fr. 709,184 (1931); Chalkley, *J. Am. Chem. Soc.*, **51**, 2489-2495 (1929).

per cent has been obtained, porous silica being used as a catalyst. Figure 10 shows a type of apparatus that may be used for this purpose.

By proper treatment, the catalyst has an indefinite life. The process, of course, is continuous, and the phenol is recovered by fractional condensation.

Manufacture of Phenol by Regenerative Process.[1]—The regenerative or Raschig process for the production of phenol is based on a combination of two well-known processes:

1. The production of chlorobenzene from benzene and hydrogen chloride and air (see Chap. IV).
2. The hydrolysis of chlorobenzene with water vapor in the presence of a catalyst.

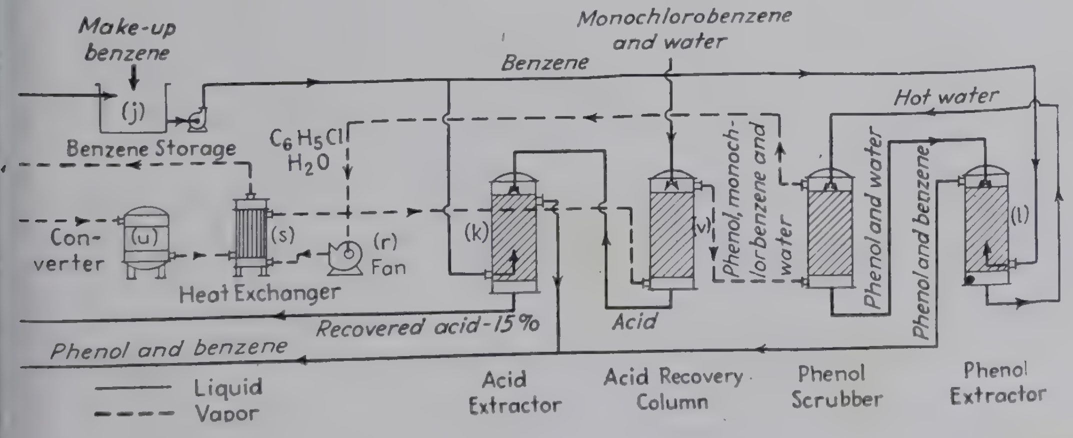
An examination of the reactions that are involved show that the by-products obtained in one step are used in the other, thus:

$$C_6H_6 + HCl + O \xrightarrow[\text{Catalyst}]{\text{Cu-Fe}} C_6H_5Cl + H_2O \qquad (1)$$

$$C_6H_5Cl + H_2O \xrightarrow[\text{Catalyst}]{SiO_2} C_6H_5OH + HCl \qquad (2)$$

In the first step, hydrogen chloride is consumed and water is produced; in the second, water is consumed and hydrochloric acid is produced. It is clear, therefore, that by a suitable combination of the two steps, phenol can be produced in a most economical manner by the consumption of only benzene and atmospheric oxygen,

$$C_6H_6 + O \rightarrow C_6H_5OH \qquad (3)$$


Make-up benzene
Monochlorobenzene and water
Benzene
Hot water
(j)
Benzene Storage
C6 H5 Cl
H2O
Con-verter
(u)
(s)
(r)
Fan
Heat Exchanger
(k)
(v)
Phenol, monochlorbenzene and water
Phenol and water
Phenol and benzene
(l)
Recovered acid-15%
Acid
Phenol and benzene
Liquid
Vapor
Acid Extractor
Acid Recovery Column
Phenol Scrubber
Phenol Extractor

phenol process.

In addition to the pronounced economy in materials, there is a further advantage in that the process permits a most economical utilization of fuel, steam, and cooling water.

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[1] This process is covered by a number of patents, in particular U. S. 1,963,761 and 2,035,917, which are assigned to F. Raschig, G.m.b.h. In the United States, the process is controlled and operated by Durez Plastics and Chemicals Corporation.

In recovering the hydrogen chloride from the hydrolytic step, it is essential to use only a limited quantity of water in the washing operations so that the hydrochloric acid is obtained as a 17 per cent solution, which is suitable for the subsequent step involving the halogenation of benzene.

The process consists of two vapor-phase catalytic stages that are fundamentally simple but become complex in practice owing to the need for separating and recovering unreacted materials and the regenerated hydrochloric acid that circulates in the process.[1] In the first stage, benzene is reacted with air and hydrochloric acid to form monochlorobenzene and water. In the second, the monochlorobenzene is reacted with steam to regenerate the HCl and produce phenol.

It may be considered that the process starts with the vapor superheater (Fig. 11) *a* near the center of the flow sheet. Benzene vapor, HCl, and air mixed in *c* are drawn into a converter *d* by suction of fan *h* at the proper temperature for reaction. The chlorobenzene formed (with a small amount of polychlorobenzenes) condenses in a partial condenser *e*, while the unreacted benzene condenses and returns to the process in a final condenser *g*. The monochlorobenzene after purification is vaporized into the second stage of the process, where it circulates with steam through a series of towers, heat exchangers *s*, a superheater *t*, and a converter *u*, in the last being in part hydrolyzed to phenol and HCl. The HCl is condensed in a partial condenser *v*, then extracted with benzene at *k* to remove what phenol it carries and returned to the first-stage process to be revaporized at *b*. The phenol in circulation is first dissolved in water in a scrubber *q*, then extracted by benzene from the water in *l*, the water returning to the scrubber *q* for further duty. The combined benzene extracts of phenol are pumped to a fractionating column *m* in the first stage where the benzene is vaporized for the first-stage process, while the crude phenol is discharged for final two-stage distillation to produce the finished product.

In the first stage, polychlorobenzenes are produced along with small quantities of CO_2 and CO. Dichlorobenzenes are formed to the extent of 6 per cent of the weight of pure phenol produced. This product is sold in the crude state to producers of para and ortho dichlorobenzenes and has a composition approximating 52 per cent para, 45 per cent ortho, and 3 per cent polychlorobenzenes. The loss in chlorine in the form of dichlorobenzenes sold constitutes part of the make-up HCl purchased for the process. In the second stage, polyphenyl compounds are formed and recovered to the extent of 2 per cent of the weight of pure phenol produced.

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[1] According to Olive, *Chem. Met. Eng.*, **47**, 770–775, 789–792 (1940), with supplementary information by R. M. Crawford, Durez Plastics and Chemicals Inc.

This product is used in the preparation of a special resin. In addition to diphenylene oxide, tetraphenylene oxide has been identified in this product. Operating in a closed cycle, the hydrochloric acid picks up impurities so that part of it must be purged continuously. This loss and that involved in the production of polychlorobenzenes constitute the replacement requirements of acid.

CHAPTER XII

THE FRIEDEL—CRAFTS REACTION

By P. H. Groggins

INTRODUCTION

In 1877, Charles Friedel and James Mason Crafts showed tha anhydrous aluminum chloride could be used as a condensing agent in "general synthetical method for furnishing an infinite number of hydrocarbons and even oxygenated compounds." They subsequently foun that ferric and zinc chlorides as well as the double salt sodium-aluminu chloride could also be employed but that these were less reactive tha aluminum halides.

Ordinarily, aluminum chloride is used to carry out the various syntheses because it is efficient and cheap. Aluminum bromide, because of it greater solubility in many organic solvents, finds many applications particularly in research work. The halides of aluminum, iron, zinc boron, tin, titanium, bismuth, and antimony have also been employe industrially either alone or in combination. Certain combinations o such Friedel-Crafts catalysts may—because of their lesser activity— ameliorate the intensity of some reactions, whereas other combination that enter into chlorination reactions result in the liberation of mor hydrogen chloride and thus accelerate certain reactions, particularl those involving olefins.

Reactions made possible through the catalytic intervention of meta halides permit the synthesis of practically all types of compounds The more important reactions are set forth in the classification o page 721.

Many of these syntheses are beyond the purview of the original report of Friedel and Crafts, and some of the new and important development bear names that testify to the inventive genius of the investigators Because the technical and patent literature generally associates th diverse developments with the original work, the term *Friedel-Craft Syntheses* is here used to encompass the reactions catalyzed by th previously mentioned metal halides.

Friedel and Crafts made their original observations on a reactio

CLASSIFICATION OF FRIEDEL-CRAFTS SYNTHESES

1. Alkylation reactions:
    - *a.* Alkylaryl compounds.
    - *b.* Alkylphenols.
    - *c.* Alkyl furoates.
    - *d.* Paraffins.
2. Synthesis of ketones:
    - *a.* Aliphatic ketones.
    - *b.* Alkyl aryl ketones.
    - *c.* Aromatic ketones.
    - *d.* Ring ketones.
    - *e.* Open diketones.
    - *f.* Keto acids.
    - *g.* Ketimides.
    - *h.* Ureas.
3. Preparation of carboxylic acid derivatives:
    - *a.* By action of phosgene.
    - *b.* By action of CO_2 and CO.
    - *c.* From cyaphenines.
4. Aldehyde syntheses.
5. Synthesis of formals.
6. Synthesis of arylalkanols.
7. Reactions of nitro compounds.
8. Preparation of primary and secondary amines.
9. Preparation of halogeno compounds:
    - *a.* Alkyl chlorides.
    - *b.* Alkylene chlorides.
    - *c.* Acid chlorides.
    - *d.* Aromatic halogeno compounds.
10. Dehydration reactions.
11. Preparation of compounds containing phosphorus, sulfur, and arsenic.
12. Isomerization reactions:
    - *a.* Alkylaromatics and alkylphenols.
    - *b.* Chloroalkenes.
    - *c.* Cycloparaffins.
    - *d.* Paraffins.
13. Polymerizations:

    Polymers and copolymers of olefins, diolefins.

Many of the syntheses noted above have played an important role during the course of the war rgency. The production of "Butyl" and "Buna S" synthetic rubbers depend on the Friedel-fts reaction. The production of aviation gasoline and lubricants also is geared to the use of metal des. These and other developments will continue to serve humanity during the postwar period.

involving the replacement of hydrogen in an aliphatic compound, *i.e.* amyl chloride,

$$C_5H_{11}Cl + C_5H_{11}Cl \xrightarrow{Al} C_{10}H_{21}Cl + HCl$$

Although numerous similar syntheses have subsequently been reported, the preparation of aliphatic compounds by the intervention o metal halides has been of minor industrial importance until the recen development of processes for the isomerization of paraffins, cycloparaffins, and olefins. These developments stem largely from advances made in the production of relatively pure aliphatic hydrocarbons and thei utilization for motor fuels[1] and for numerous syntheses by the chemica industry.[2]

Most of the industrially useful Friedel-Crafts reactions involve th union of a comparatively active compound with a relatively stabl aromatic hydrocarbon or substituted hydrocarbon in the presence of a metal halide. For purposes of elucidation, benzene is used as the relatively stable hydrocarbon and aluminum chloride as the metal halide i the general reactions shown on page 723. Reactions of this type involving one-ring nucleus such as benzene, phenol, and naphthalene ordinaril lead to high yields of desired specific product.

Clearly, other alkyl or aralkyl halides, *e.g.*, isopropyl chloride o *p*-chlorobenzyl chloride, can be substituted for the illustrative side-chai halides. Similarly, other acid chlorides, carboxylic acid anhydrides, etc. can be employed in comparable syntheses. Finally, other cyclic o heterocyclic compounds can replace benzene. It is to be emphasized therefore, that the preceding are merely type reactions, and the development of similar syntheses is limited only by the vision and ingenuity o the investigator.

By and large, the orientation of substituents introduced by means o the Friedel-Crafts reaction is the same as other aromatic substitutio reactions. *e.g.*, nitration and halogenation. The exceptions relat largely to alkylation reactions wherein the alkyl halides may migrate o undergo rearrangement to the most highly branched alkyl groups. Th tendency to give unexpected results is accentuated by increased temperature, abnormal proportions of reactants, or the presence of catalyzin substances.

Because reactions catalyzed by metal halides may involve simpl addition, double decomposition, polymerization, hydrogenation an

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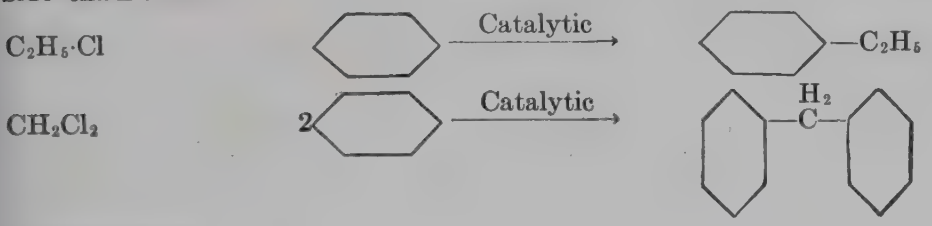
[1] The reader is referred to the numerous technical reports by Ipatieff and hi colleagues for detailed developments in this field. See also references in sections o this chapter dealing with alkylation and isomerization.

[2] The classic work of Thomas, "Anhydrous Aluminum Chloride in Organi Chemistry," *Am. Chem. Soc. Monograph* 87, is suggested as a reference book.

TYPES OF FRIEDEL-CRAFTS SYNTHESES

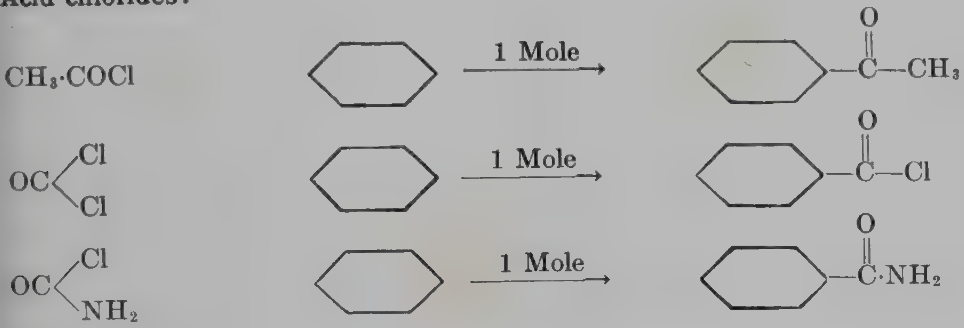
Active Compound | Relatively Stable Hydrocarbon | $AlCl_3$ | Product

Side-chain halides:



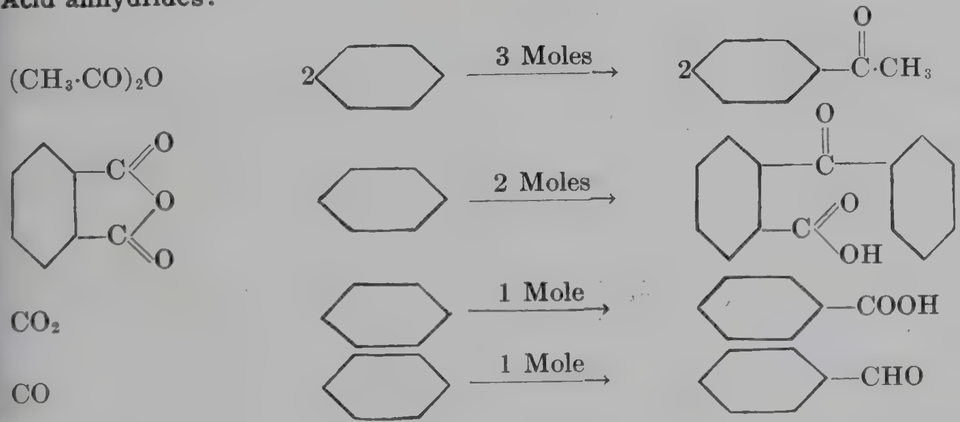
$C_2H_5 \cdot Cl$
Catalytic
$—C_2H_5$
CH_2Cl_2
2
Catalytic
H_2
C

Acid chlorides:



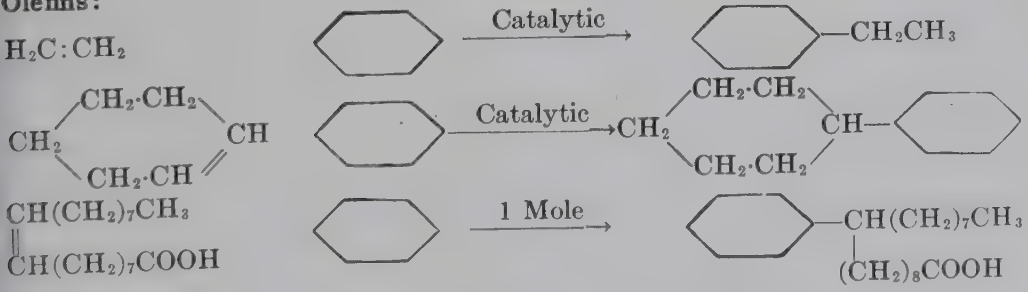
$CH_3 \cdot COCl$
1 Mole
O
C—CH_3
OC
Cl
Cl
1 Mole
O
C—Cl
OC
Cl
NH_2
1 Mole
O
C·NH_2

Acid anhydrides:



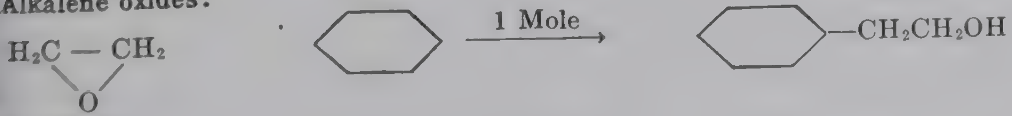
$(CH_3 \cdot CO)_2O$
2
3 Moles
2
O
C·CH_3
C
O
O
C
O
2 Moles
O
C
C
O
OH
CO_2
1 Mole
—COOH
CO
1 Mole
—CHO

Olefins:



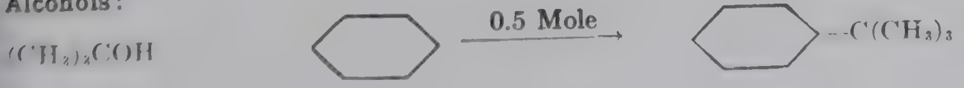
$H_2C:CH_2$
Catalytic
$—CH_2CH_3$
$CH_2 \cdot CH_2$
CH_2
CH
$CH_2 \cdot CH$
Catalytic
CH_2
$CH_2 \cdot CH_2$
CH—
$CH_2 \cdot CH_2$
$CH(CH_2)_7CH_3$
$CH(CH_2)_7COOH$
1 Mole
$—CH(CH_2)_7CH_3$
$(CH_2)_8COOH$

5. **Alkalene oxides:**



$H_2C — CH_2$
O
1 Mole
$—CH_2CH_2OH$

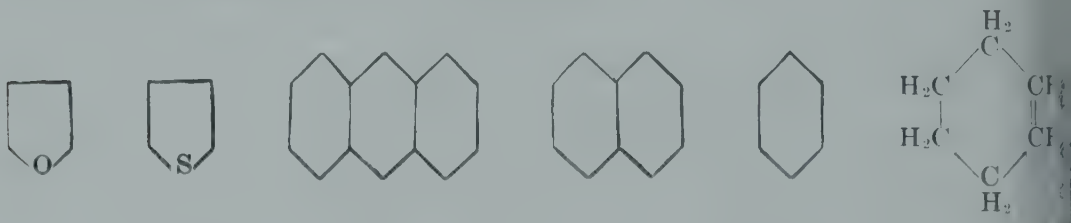
Alcohols:



$(CH_3)_3COH$
0.5 Mole
$—C(CH_3)_3$

dehydrogenation, chlorination and dehydrochlorination, dehydration, isomerization, fission, inter- and intramolecular rearrangements, etc., it is not at all surprising that abnormalities do occur when aluminum chloride is employed as a catalytic activating or condensing agent. These exceptions, however, serve only to emphasize the large body of normal dependable and technically useful Friedel-Crafts syntheses. These include, in addition to the general reactions involving the use of aromatic compounds, the isomerization of paraffins and cycloparaffins, the condensation of olefins with paraffins, the preparation of alkyl and aryl halides, and the formation of acyl halides and aliphatic ketones.

According to Calloway the relative ease with which unsubstitute rings undergo substitution by means of the Friedel-Crafts reaction in the order of decreasing activity is as follows:[1,2]



For the substituted nuclei, the influence of groups on the order o activity is usually as follows, the activity decreasing from left to right:

$$-OH \text{ and } -OCH_3,\ (CH_3)_2N-,\ CH_3-,\ H-,\ \left\{\begin{array}{l} Cl- \\ Br-, \\ I- \end{array}\right.\ \left\{\begin{array}{l} -CHO \\ \\ -COCH_3 \end{array}\right.,$$

In general, an increasing electronegativity or "acidity" of the grou increases the difficulty of substitution.

ALKYLATION REACTIONS

General Comments.—Alkylations can be effected with alkyl, aralkyl and cycloparaffinic halides, olefins, alcohols, and esters. In practicall all instances, hydrogen chloride is a product of the reaction and it ma reasonably be presumed that olefins, esters, and in many instance alcohols are first transformed into alkyl halides before entering into th alkylation reaction.[3]

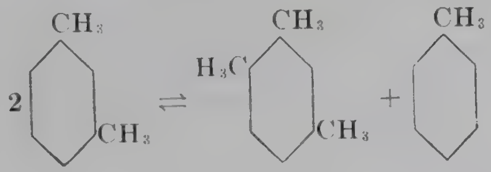
---

[1] Calloway, *Chem. Rev.*, **17,** 327 (1935).

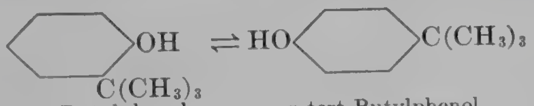
[2] Unsubstituted furan undergoes acylation readily but has not been alkylate Aluminum chloride is highly efficient in alkylating substituted furans, but stann and ferric chlorides are more efficient in the acylation of furans.

[3] An apparent exception is *n*-propyl alcohol which probably initially form $C_3H_7OAlCl_2$. See Ipatieff, Pines, and Schmerling, *J. Org. Chem.*, **5,** 253 26 (1940).

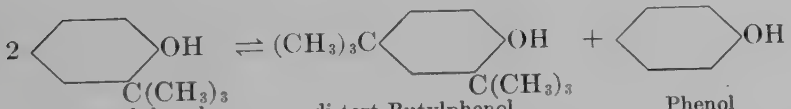
Alkylation reactions are in general reversible. Thus, xylene yields uene and trimethylbenzene when treated with aluminum chloride.



Similar equilibriums exist in the formation of tertiary butylphenols:



o-tert-Butylphenol *p*-tert-Butylphenol



o-tert-Butylphenol di-tert-Butylphenol Phenol

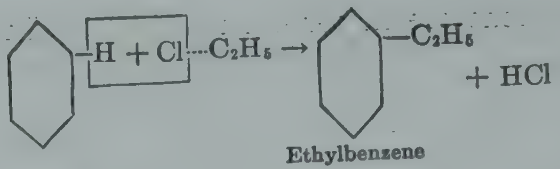
These equilibriums have been shown to be a function of the temperaıre of the reaction and are influenced by the concentration of the ·actants.

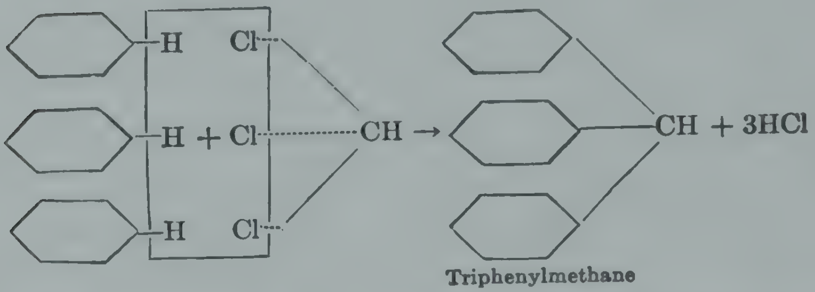
Except when alcohols and esters are used as alkylating agents, the kylation reactions require only catalytic quantities of aluminum ıloride as a catalyst. This is attributed to the formation of an unstable ›mplex of aluminum chloride with the reactants and its liberation for ırther activity upon completion of the alkylation reaction.

From the type reactions set forth on page 723, it can be seen that ıere is a definite relationship between the "active" compound and the uantity of $AlCl_3$ required. When the active component forms a ·latively stable binary complex, *e.g.*, > CO:$AlCl_3$, at least molar proortions of aluminum chloride are required in order to obtain approxiıately theoretical yields.

Attention is called to the fact that all the active compounds with ɦe exception of carbon monoxide, olefins, and alcohols undergo hydrolyis and ammonolysis without benefit of catalysts. In the light of known elationships in such unit processes, it is appropriate to accept the coniderable body of evidence regarding the conversion of olefins and ertiary alcohols to alkyl halides as a precursor to reaction.

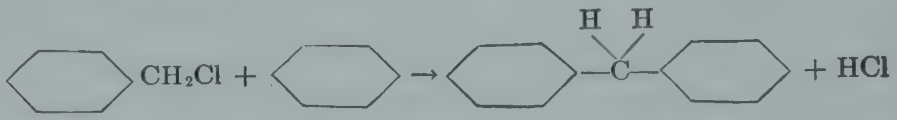
Alkylaryl Compounds.—The following reactions illustrate the formaion of alkyl aryl compounds through the interaction of alkyl halides and ıromatic compounds. The double decomposition involves the eliminaion of hydrogen chloride, the hydrogen atom being linked to a carbon n a ring, while the halogen atom may be linked to a carbon atom in an ılkyl, aralkyl, or cycloparaffinic halide.


H + Cl
C₂H₅ →
C₂H₅
+ HCl
Ethylbenzene

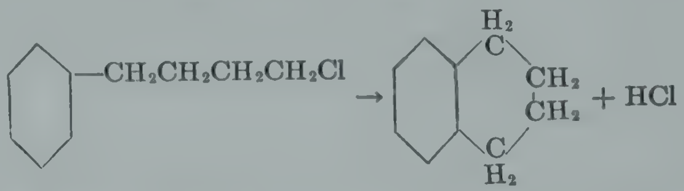

H
Cl
H + Cl
CH →
H
Cl
CH + 3HCl
Triphenylmethane

It is to be emphasized that instead of the illustrative alkyl halide other similar compounds such as isopropyl chloride, allyl chloride, o kerosene chloride may be used. Instead of benzene, other aromati compounds such as toluene, chlorobenzene, and naphthalene may b employed.

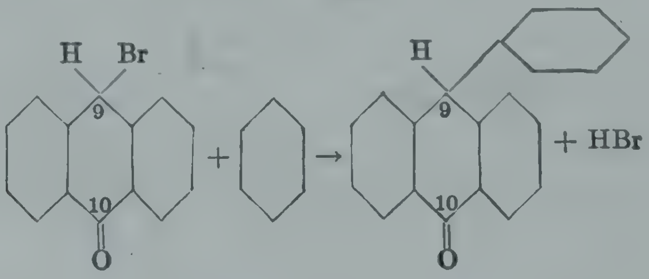
Aralkyl chlorides react in the same manner as do alkyl halides Diphenylmethane is thus obtained by the condensation of benzyl chloride with benzene:


CH₂Cl +
→
H H
C
+ HCl

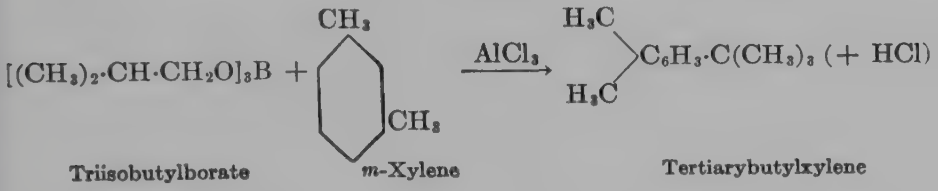
When the aliphatic chain of an aralkyl halide is sufficiently long, a inner ring closure is effected by anhydrous aluminum chloride. In thi way, 1-phenyl-4-chlorobutane yields tetralin:


CH₂CH₂CH₂CH₂Cl
→
H₂
C
CH₂
CH₂
C
H₂
+ HCl

Although halogenobenzenes do not condense with the loss of haloge from the ring, an anthrone containing halogen in the meso position i capable of reacting with benzene with the loss of halogen, 9-phenylanthrone being obtained in this manner:

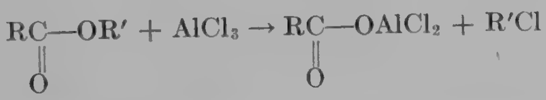

H Br
9
10
O
+
→
H
9
10
O
+ HBr

In the preparation of hydrocarbons according to the Friedel-Crafts eaction, alkyl halides may be replaced by alkyl borates or aralkyl borates. he following is a typical reaction:



The borates are formed practically quantitatively by simply heating he alcohol with boric acid, water being eliminated during the process. The trialkyl borates possess a higher boiling point than the corresponding lkyl chlorides, *e.g.*, C_2H_5Cl (b.p., 12°C.); $(C_2H_5O)_3B$ (b.p., 112°C.). This characteristic permits of a simple control of their purity by distillaion. Unusually high yields of hydrocarbon, *i.e.*, 80 to 90 per cent of the heoretical, are claimed for the process. The quantity of higher boiling ractions is small, while the formation of resinous products is negligible.

Alkyl sulfates and carbonates have been employed for the alkylation of hydrocarbons.[1] Such processes give only mediocre yields of alkyl



$$R\underset{\underset{O}{\|}}{C}-OR' + AlCl_3 \rightarrow R\underset{\underset{O}{\|}}{C}-OAlCl_2 + R'Cl$$

derivative and, in addition, require a ratio of 1.5 moles $AlCl_3$ per mole of alkyl ester undergoing condensation.

In place of saturated aliphatic halides, *olefins* in conjunction with hydrogen chloride may be used as alkylating agents. When an olefin reacts with hydrogen chloride in the presence of aluminum chloride, the corresponding alkyl chloride is formed. Thus ethylene may, and in industrial operations does, replace ethyl chloride in the synthesis of ethylbenzene, since the former is converted to ethyl chloride during the course of the reaction.

$$H_2C{:}CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl \xrightarrow{AlCl_3} [CH_3\overset{+}{C}H_2 \cdots Al\overset{-}{Cl_4}]$$

$$[CH_3\overset{+}{C}H_2 \cdots Al\overset{-}{Cl_4}] + C_6H_6 \rightarrow CH_3 \cdot CH_2 \cdot C_6H_5 + HCl + AlCl_3$$

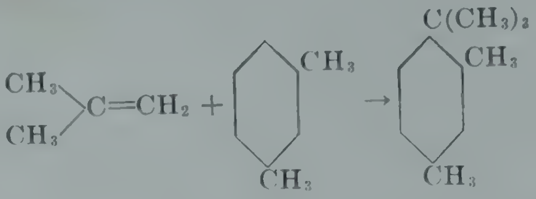
It has been shown by Fairbrother that in the negative $AlCl_4$ ion, any one of the chlorine atoms has an equal chance of being liberated with the evolved hydrogen chloride.[2]

---

[1] KANE and LOWY, *J. Am. Chem. Soc.*, **58**, 2605 (1936). Under some conditions esters of carboxylic acids act as alkylating agents. This may be owing to the preliminary formation an alkyl halide

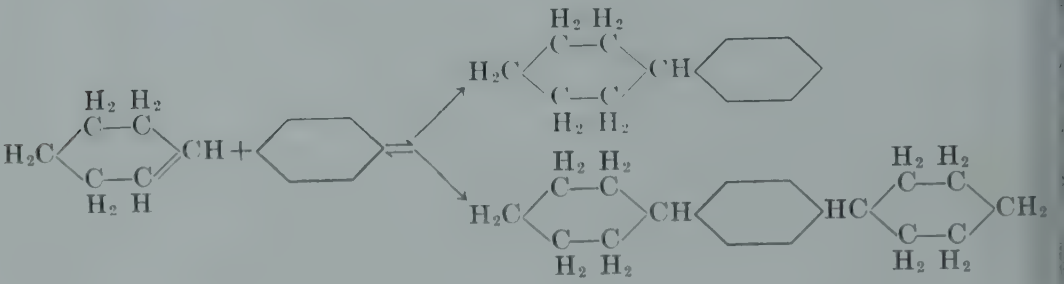
[2] FAIRBROTHER, *J. Chem. Soc.*, **1937**, 503.

In a similar manner, isobutylene condenses with *m*-xylene to form dimethyl-*tert*-butylbenzene.

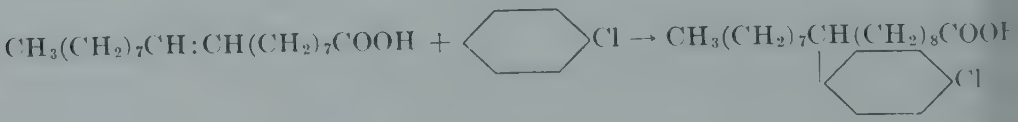


Although aluminum chloride catalyzes the formation of ethyl chloride from ethylene, it is not satisfactory in causing the conversion of amylene to amyl chloride because of loss through polymerization. On the othe hand, amylene can be used in a typical Friedel-Crafts synthesis, becaus the amyl aluminum tetrachloride promptly combines with aromatic hydrocarbons that may be present.

Cyclohexene reacts with benzene to form mono- to tetracyclohexylbenzenes, depending on the proportions of cyclohexene present.[1] Th reaction is reversible, and the cyclohexyl groups in polycyclohexylbenzenes can be transferred to benzene.[2]



Similar reactions involving unsaturated fatty acids lead to aryl-stearic acids. The preparation of 9- or 10-chlorophenyloctadecanoi acids from oleic acid and chlorobenzene may be represented thus:



In contrast to the other condensations of olefins to yield hydrocarbons this synthesis, because of the presence of the carboxyl group, requires slight excess over 1 mole $AlCl_3$ instead of the usual catalytic quantities The mechanism of addition is, however, similar to that of olefins an probably proceeds as follows:

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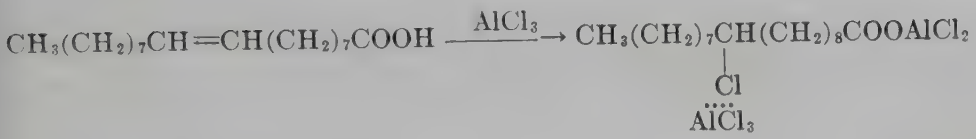
[1] U. S. 1,969,984 (1936).

[2] Corson and Ipatieff, *J. Am. Chem. Soc.*, **59**, 645 (1937).



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow{AlCl_3} CH_3(CH_2)_7\underset{\underset{\vdots}{\overset{|}{Cl}}\atop AlCl_3}{CH}(CH_2)_8COOAlCl_2$$

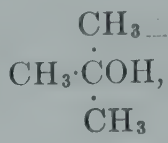
t is clear, therefore, that 1 mole $AlCl_3$ is needed to form the addition complex and a slight excess is desirable to produce the active, positive $CH_3—\overset{+}{C}H—COOAlCl_2$ and negative $Al\overset{-}{Cl_4}$ ions. These presumably form a ternary complex with benzene leading to the formation of the arylstearic acid.

Aliphatic alcohols react with aromatic compounds in the presence of aluminum chloride to form alkyl aryl compounds. The reactivity of the aliphatic alcohols increases in the order primary, secondary, tertiary. Primary and secondary alcohols require greater $AlCl_3$ ratios and higher reaction temperatures than do tertiary alcohols.

According to Norris and Sturgis, 1 mole of ethyl alcohol reacts with 1 mole of $AlCl_3$ to form a binary complex which, in the presence of HCl, yields ethyl chloride:[1]

$$C_2H_5OH + AlCl_3 \rightarrow C_2H_5OH{\cdot}AlCl_3 \rightarrow$$
$$HCl + C_2H_5O{\cdot}AlCl_2 \rightarrow C_2H_5Cl + AlOCl$$

The addition product $C_2H_5OH{\cdot}AlCl_3$ is formed at room temperature, and, upon heating, nearly a quantitative yield of ethyl chloride is obtained. The reaction is, however, general and can be facilitated by the introduction of hydrogen chloride which serves to esterify the alcohol. The butyl, amyl, and longer chain alcohols, depending on the position of the —OH group, may become more highly branched; thus a *n*-butyl becomes a secondary butyl alkyl group owing to a hydrogen shift.

Huston and coworkers in a succession of reports have shown that when alcohols are employed as alkylating agents, it is important to give particular attention to the $AlCl_3$ ratio and the reaction temperature; otherwise the yields of alkyl derivatives are low.[2] Roughly, the $AlCl_3$ requirements are as follows: primary alcohol, 1 mole; secondary alcohol, 0.75 mole; and tertiary alcohol, 0.5 mole. When too low a reaction temperature is used in condensing primary and secondary alcohols, the yields are correspondingly low. When the alcohol has a neopentyl group as in *tert*-butyl alcohol,  $CH_3\cdot\overset{CH_3}{\underset{CH_3}{C}}OH$, excessive temperatures lead to secondary reactions. Thus Norris and Sturgis obtained an 84 per cent yield of *tert*-butylbenzene by adding 0.6 mole $AlCl_3$ to an agitated mixture consisting of 0.5 mole of the alcohol and 3 moles of benzene kept at 0°C. and then allowing the reaction mass to stand at room temperature for 20 hr.[1] When the same proportions of reactants are heated for 6 hr. at 80°C. and then for 2 hr. at 95°C., no *tert*-butylbenzene is formed. Instead the product consists of toluene, ethylbenzene, and isopropylbenzene.

---

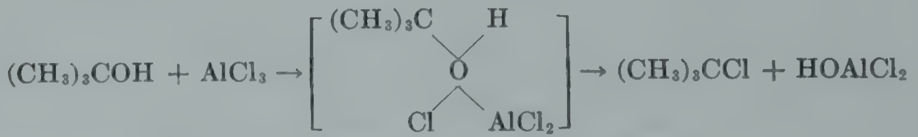
[1] NORRIS and STURGIS, *J. Am. Chem. Soc.*, **61**, 1413 (1939).

[2] HUSTON and HSIEH, *J. Am. Chem. Soc.*, **58**, 439 (1936); HUSTON, FOX, and BINDER, *J. Org. Chem.*, **3**, 251 (1938); HUSTON and HEDRICK, *J. Am. Chem. Soc.*, **59**, 2001 (1937); HUSTON and GUILE, *J. Am. Chem. Soc.*, **61**, 69 (1939); HUSTON and KAYE, *J. Am. Chem. Soc.*, **64**, 1576 (1942); HUSTON and MELOY, *J. Am. Chem. Soc.*, **64**, 2655 (1942).

Cycloaliphatic alcohols and *aralkyl alcohols* may also be used as alkylating agents. Thus cyclohexanol can be condensed with benzene to give a 62 per cent yield of cyclohexylbenzene and a 35 per cent yield of a mixture of di- and tricyclohexylbenzenes. Similarly, benzyl alcohol and phenols react to form benzylphenols. In general, the aralkyl alcohols give relatively poor results as alkylating agents.

Preparation of Alkylphenols.—The methods that are usually employed for the preparation of hydrocarbons are suitable also for the alkylation of phenols. As a rule, phenols undergo alkylation under milder conditions and frequently enter into reactions where benzene is almost unreactive. In addition to alkyl and aralkyl esters and olefins, primary, secondary, and particularly tertiary alcohols can be condensed with mono- and dihydric phenols by the use of aluminum chloride.[2]

The reaction mechanism for the preparation of *tert*-butylphenol from *tert*-butyl alcohol and phenol is not known but may be as follows:



(1)

$$(CH_3)_3CCl + C_6H_5OH \xrightarrow{AlCl_3} (CH_3)_3C\cdot C_6H_4OH + HCl \qquad (2)$$

The mechanism of reaction is undoubtedly more complex. In all probability the hydrogen chloride that is liberated [Eq. (2)] serves to convert some of the residual alcohol to the chloride, which accounts for the need of only about 0.5 mole $AlCl_3$ per mole of *tert*-butyl alcohol. The intermediate formation of the reactive alkyl chloride can easily be demonstrated.[1] When *tert*-butyl alcohol (b.p., 82.8°C.) is gradually

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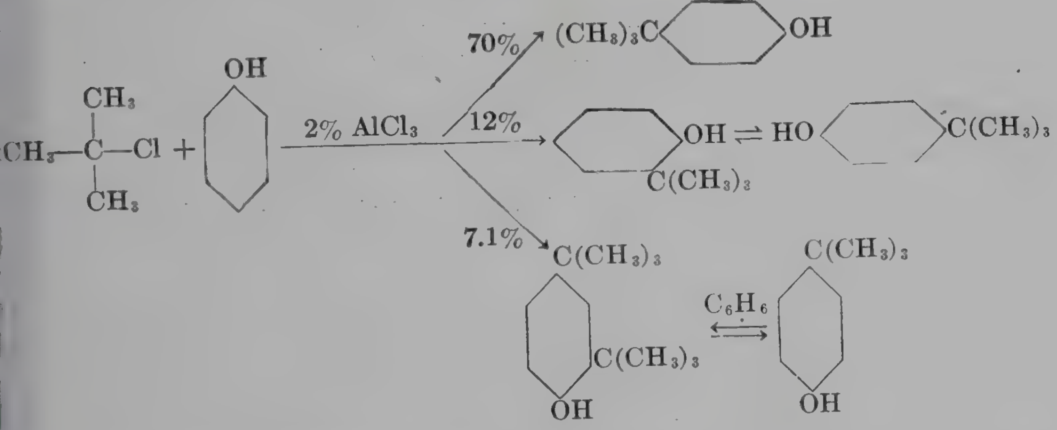
[1] NORRIS and STURGIS, *J. Am. Chem. Soc.*, **61**, 1413 (1939).

[2] Huston, U. S. 2,051,300 (1936); HUSTON and HSIEH, *J. Am. Chem. Soc.*, **58**, 439 (1936). TSUKERVANIK and NAZAROVA, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 767 (1936); see also references on p. 729.

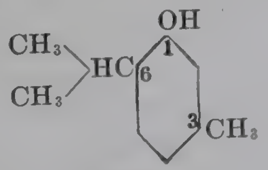
$$(CH_3)_3COH \xrightarrow{AlCl_3} (CH_3)_2C{=}CH_2 \xrightarrow{HCl} (CH_3)_3CCl$$

added to a suspension of aluminum chloride in nitrobenzene at 70°C., *ert*-butyl chloride (b.p., 51°C.) distills over. These observations point to the desirability of working under a slight hydrogen chloride pressure and of fitting the reactor with an efficient reflux condenser.

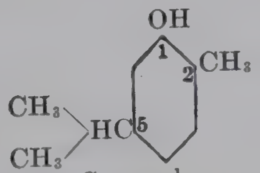
When a *tert*-alkyl halide, *e.g.*, *tert*-butyl chloride, is condensed with a phenol in which the 2 and 4 positions are free, there is formed 4-*tert*-butylphenol as the principal product along with appreciable quantities of 2-*tert*- and 2, 4-di-*tert*-butylphenol.[2]



Thymol and carvacrol, which are important antiseptics, can be synthesized by reacting equivalent quantities of isopropyl chloride with *m*- and *o*-cresols, respectively, at −10°C. in the presence of a solvent.[3] In contrast to the synthesis of butylphenol which requires only catalytic quantities of aluminum chloride, at least molar equivalents of the condensing agent are employed in this reaction.



Thymol



Carvacrol

When initial and final temperatures of 20 and 60°C., respectively, are used in the condensation of *m*-cresol, the product is not thymol, but the isomeric 3-methyl-5-isopropylphenol. Likewise, in the carvacrol synthesis, there is obtained about 15 per cent of the isomeric 2-methyl- isopropylphenol when the reaction temperature is as low as −15°C.

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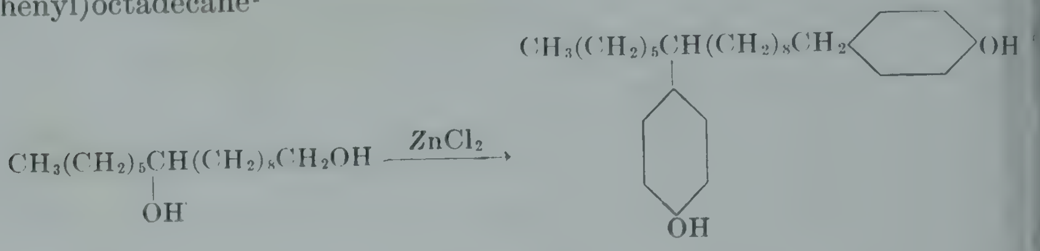
[1] GROGGINS and SWERN, Unpublished investigations, 1937. The initial formation of an olefin which adds HCl to form the same alkyl chloride is of course not excluded.

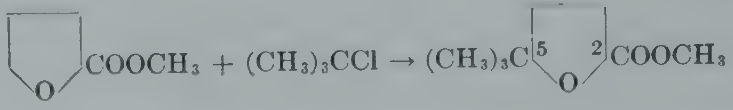
[2] Perkins *et al.*, U. S. 1,972,599 (1934).

[3] Carpenter, U. S. 2,064,885 (1936); U. S. 2,286,953 (1942).

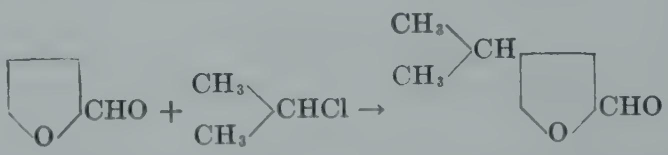
Long-chain polymethylene hydroxides also react with phenols. Thu 1,10-octadecanediol condenses with phenol to yield 1,10-di(hydroxy phenyl)octadecane[1]



Alkylation of Furoates.—Although no direct alkylation of fura occurs, methyl 2-furoate undergoes alkylation to yield methyl 5-alkyl- furoates.[2]



Normal, iso- and *sec*-butyl halides can be used in the above reactio but the product, however, is always the most highly branched methy 5-*tert*-butyl-2-furoate. Furfural similarly undergoes alkylation, but surprisingly, the new substituent goes into the 4- instead of the expecte 5- position.[3]



Alkylation of Paraffins.—Ipatieff and coworkers showed that th addition of paraffins to olefins is a general but complex reaction whicl takes place readily.[4] When aluminum chloride is used as the catalyst secondary alkylation reactions as well as side reactions occur.

Komarewsky and Warson, in reviewing the progress made in th alkylation of paraffins and cycloparaffins by olefins, point out that th reactions are beset by (1) the phenomenon of destructive alkylation, (2 omerization, (3) intra- and intermolecular hydrogenation-dehydrogena-on, and (4) conjunct polymerization.[1]

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[1] U. S. 2,321,620 (1943).

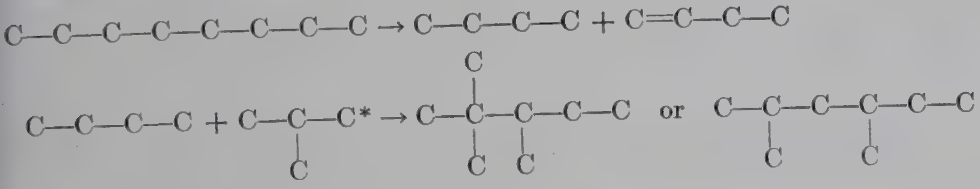
[2] Gilman and Calloway, *J. Am. Chem. Soc.*, **51,** 4197 (1933).

[3] Gilman, McCorkle, and Calloway, *J. Am. Chem. Soc.*, **56,** 745 (1934).

[4] Ipatieff and Grosse, *J. Am. Chem. Soc.*, **57,** 1616 (1935); **58,** 915 (1936) Ipatieff, Grosse, Pines, and Komarewsky, *J. Am. Chem. Soc.*, **58,** 913 (1936) Ipatieff and Pines, *Ind. Eng. Chem.*, **27,** 1364 (1935); Ipatieff and Schaad, *Ind Eng. Chem.*, **37,** 326 (1945).

These reactions are usually accompanied by the formation of two yers. The upper layer contains hydrocarbons, and the lower layer ontains the so-called aluminum chloride-hydrocarbon complex. The ower layer, on decomposition with water, forms aluminum hydroxide, ydrogen chloride, and a highly unsaturated hydrocarbon layer. In racking of natural hydrocarbon mixtures in the presence of aluminum hloride, two facts are apparent: The product in the upper layer is satu-ated, and isoparaffins are the principal upper-layer hydrocarbons. These products can readily be explained by the reactions mentioned bove. Thus, any hydrocarbon decomposing under the action of alumi-um chloride and forming unsaturated fragments will form a saturated roduct by the processes of alkylation, intermolecular dehydrogenation-ydrogenation, and conjunct polymerization. For example,

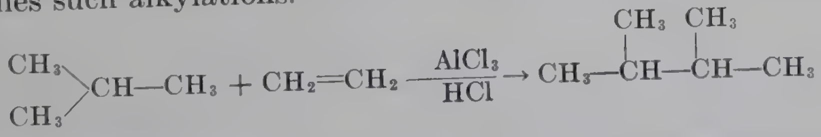
Paraffin Hydrocarbons.



$$\mathrm{C{-}C{-}C{-}C{-}C{-}C{-}C{-}C \rightarrow C{-}C{-}C{-}C + C{=}C{-}C{-}C}$$

$$\mathrm{C{-}C{-}C{-}C + C{-}\underset{\underset{C}{|}}{C}{-}C^{*} \rightarrow C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}\underset{\underset{C}{|}}{C}{-}C{-}C \quad or \quad C{-}\underset{\underset{C}{|}}{C}{-}C{-}\underset{\underset{C}{|}}{C}{-}C{-}C}$$

The preparation of 2, 3-dimethylbutane from ethylene and isobutane exemplifies such alkylations.



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{CH{-}CH_3 + CH_2{=}CH_2 \xrightarrow[HCl]{AlCl_3} CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3}$$

When propene is used as the olefinic reactant, the products are principally 2, 3- and 2, 4-dimethylpentane. High yields of specific products are not obtainable, but this constitutes no serious problem when consideration is given to the low cost of raw materials and the utility of the products of reaction either as a starting material for organic syntheses or as a fuel.

Schmerling has shown that the alkyl halides also react with olefins.[2] On account of the ease with which such reactants enter into polymerization and other reactions, it is necessary, when an active catalyst such as aluminum chloride is used, to carry out the reaction at −30 to 0°C. A temperature range of 20 to 100° may be employed when a less active metal halide, such as zinc chloride, is used. The primary reaction is that of addition of the alkyl group and halogen atom to the double bond of the olefin, the halogen adding to the carbon atom carrying the smaller number of hydrogen atoms.

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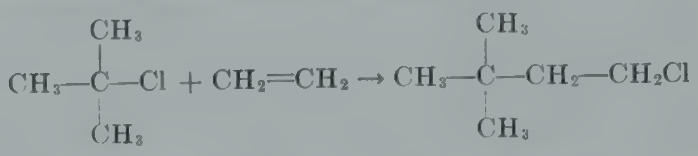
[1] Komarewsky and Warson, *J. Ind. Eng. Chem.*, **37,** 323 (1945).

* Isomerization can occur before or after fission.

[2] Schmerling, *J. Am. Chem. Soc.*, **67,** 1152 (1945).

$$RX + CH_2{=}CHR' \rightarrow R{-}CH_2{-}CHXR'$$

More specifically, the reaction of *tert*-butyl chloride with ethylene yields 1-chloro-3, 3-dimethylbutane as principal product.



$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl + CH_2{=}CH_2 \rightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}CH_2Cl$$

$AlCl_3$ in Alkylation Reactions.—During the course of alkylation reactions, the aluminum chloride catalyst is bound up with part of the organic materials undergoing reaction. This organo-aluminum chloride complex which generally settles to the bottom of the reactor has one or more unsaturated components. After separation of the organo-aluminum chloride complex from the upper saturated components, it can serve as the catalyst for subsequent alkylation or dealkylation reactions.

The principles underlying the economic use of Friedel-Crafts catalysts are briefly as follows:

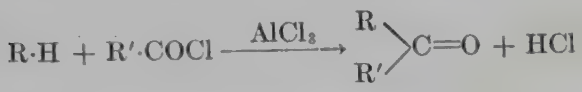
1. When alkyl halides are condensed, the catalyst can be regenerated and reused by adding aluminum powder.

2. When olefins and alcohols are condensed, the hydrogen chloride that is needed to accelerate the reaction and improve the yields can be obtained by

   a. Introducing hydrogen chloride as a coreactant.
   b. Using some corresponding alkyl halide, at least to initiate the reaction.
   c. Leaving or introducing a residue of organo-aluminum chloride complex.
   d. Using moist aluminum chloride or a metal halide to which hydrochloric acid has been added.
   c. Using moist olefin or alcohol.
   f. Using mixed metal halides, one of which as in $AlCl_3$-$FeCl_3$ is reduced more readily to a basic salt.

SYNTHESIS OF KETONES

General Remarks: Acylations.—Friedel and Crafts showed that simple ketones could be prepared by the action of aliphatic and aromatic acid chlorides on aromatic compounds. The reaction, which is general for aromatic hydrocarbons and their halogeno derivatives, phenols and phenol ethers, may be represented as follows:



$$R\cdot H + R'\cdot COCl \xrightarrow{AlCl_3} \begin{matrix}R\\R'\end{matrix}\!>C{=}O + HCl$$

Vhen acid chlorides are condensed with olefins, branched-chain paraffins, and cycloparaffins, the ketones are obtained in comparatively low yields.

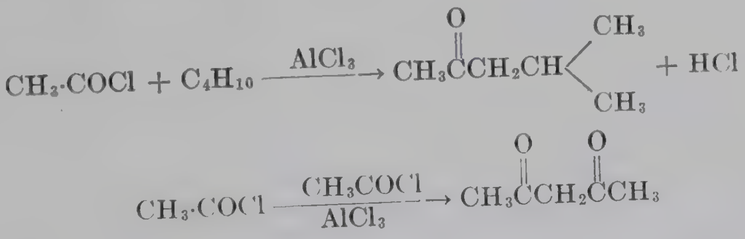
Noller and Adams[1] showed that aliphatic acid anhydrides could be substituted for acid chlorides, and Groggins and coworkers[2] have demonstrated that alkyl aryl and diaryl ketones[3] could be derived from carboxylic acids.

Because the aluminum chloride becomes bound to the carbonyl group during acylations, it is necessary to have a slight excess over stoichiometric proportions of the catalytic condensing agent. The $AlCl_3$, which initially attaches to the $>C{=}O$ group, remains bound during the entire reaction and is removed only by hydrolysis after completion of the acylation.

Electronegative substituents in aromatic nuclei have an inhibiting effect on acylations. Thus, nitrobenzene does not condense with benzoyl chloride. The retarding effect is not so pronounced in nitro-polyalkylated benzenes, phenols, or phenol ethers, where the activating influence of alkyl, hydroxy and alkoxy groups have a counter influence. Negative substituents in the acylating agent have a relatively weak inhibiting effect, and *o*- or *m*-nitrobenzoyl chloride condenses with benzene to yield the corresponding nitrobenzophenones.

The order of reactivity for acyl halides in the synthesis of ketones has been found by Calloway to be as follows: acyl iodide > acyl bromide > acyl chloride > acyl fluoride.[4]

Aliphatic Ketones.—Acyl halides have been shown to act on butane, pentane, and hexane in the presence of aluminum chloride to give low yields of ketones. The action of acetyl chloride on *n*-butane leads to the formation of some methyl isobutyl ketone as well as acetyl acetone.



$$CH_3\cdot COCl + C_4H_{10} \xrightarrow{AlCl_3} CH_3\overset{O}{\overset{\|}{C}}CH_2CH\begin{matrix}CH_3\\ \\CH_3\end{matrix} + HCl$$

$$CH_3\cdot COCl \xrightarrow[AlCl_3]{CH_3COCl} CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$$

When acid chlorides are condensed with olefins, low yields of unsaturated chloro ketones are obtained. The olefins appear to add acid chloride at the double bond initially, but the addition product is unstable and loses hydrogen chloride.

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[1] Noller and Adams, *J. Am. Chem. Soc.*, **36**, 736 (1914).

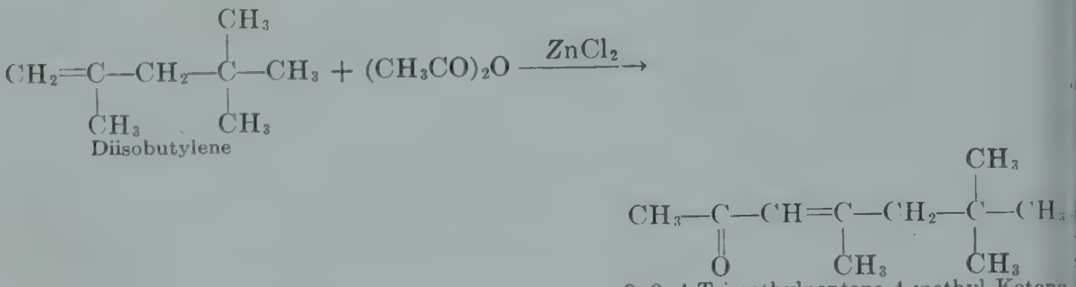
[2] Groggins, Nagel, and Stirton, *Ind. Eng. Chem.*, **26**, 1313 (1934).

[3] Newton and Groggins, *Ind. Eng. Chem.*, **27**, 1397 (1935).

[4] Calloway, *J. Am. Chem. Soc.*, **59**, 1474 (1937).

$$R{\cdot}CH{:}CH_2 \xrightarrow[AlCl_3]{R'{\cdot}COCl} R{\cdot}CHCl{\cdot}CH_2{\cdot}COR' \rightarrow R{\cdot}CH{:}CH{\cdot}COR' + HCl$$

Byrns reports that 25 per cent yields of ketone can be obtained by slowly adding a mixture of diisobutylene and zinc chloride to acetic anhydride.[1] The reaction and structure of the principal ketone obtained are as follows:

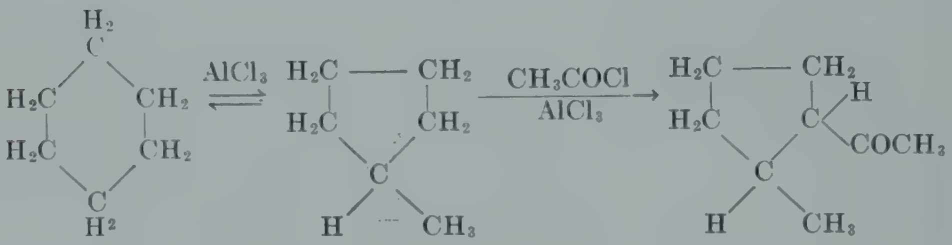


$$CH_2{=}C(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3 + (CH_3CO)_2O \xrightarrow{ZnCl_2} CH_3{-}C({=}O){-}CH{=}C(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3$$

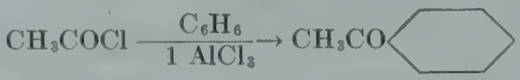
Diisobutylene

2, 2, 4-Trimethylpentene-4 methyl Ketone

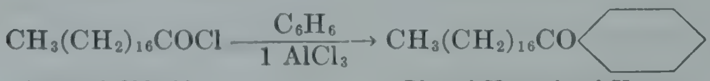
Acetyl chloride acts on cyclohexane in the presence of aluminum chloride to yield 1-methyl-2-acetylcyclopentane. According to Nenitzescu, isomerization precedes acylation as follows:[2]



Alkyl Aryl Ketones.—Alkyl aryl ketones can readily be obtained in high yields by condensing aliphatic acid chlorides, acid anhydrides, and carboxylic acids with aromatic compounds. Typical syntheses in the presence of an excess of benzene are as follows:



Acetyl Chloride — Acetophenone



Stearoyl Chloride — Phenyl Heptadecyl Ketone

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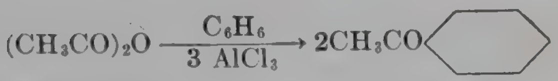
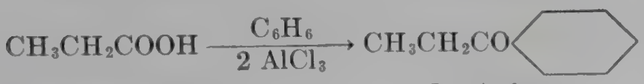
[1] U. S. 2,355,703 (1944).

[2] NENITZESCU and IONESCU, *Ann.*, **491**, 189 (1931).


(CH₃CO)₂O
C₆H₆
3 AlCl₃
2CH₃CO

Acetic Anhydride

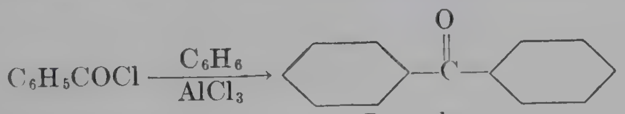
Acetophenone


CH₃CH₂COOH
C₆H₆
2 AlCl₃
CH₃CH₂CO

Propionic Acid

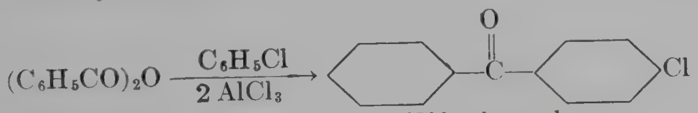
Propiophenone

Aromatic Ketones.—The reactions pertaining to the preparation of aromatic ketones are similar to those of alkyl aryl ketones. The following reactions typify the acylation of benzene and its homologues by aroyl halides, aromatic acid anhydrides, and aromatic carboxylic acids.


C₆H₅COCl
C₆H₆
AlCl₃
O
C

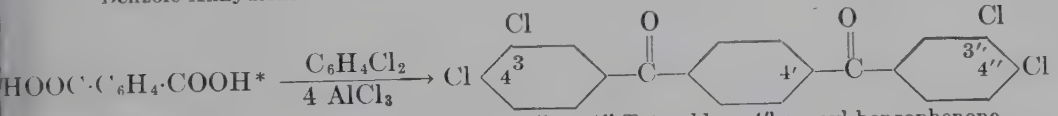
Benzoyl Chloride

Benzophenone


(C₆H₅CO)₂O
C₆H₅Cl
2 AlCl₃
O
C
Cl

Benzoic Anhydride

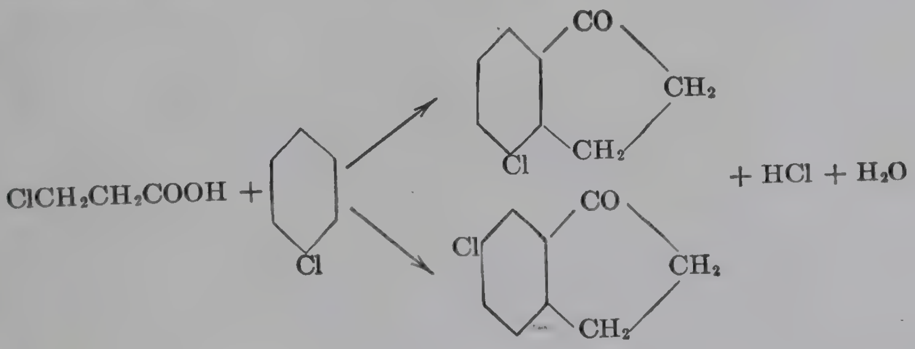
4-Chlorobenzophenone


HOOC·C₆H₄·COOH*
C₆H₄Cl₂
4 AlCl₃
Cl
Cl
4
3
O
C
4′
O
C
Cl
3″
4″
Cl

Terephthalic Acid

3, 3″, 4, 4″-Tetrachloro-4′benzoyl benzophenone

Ring Ketones.—Previously, in the preparation of tetralin from 1-phenyl-4-chlorobutane, it has been shown that an inner ring closure can be effected on aralkyl compounds when the aliphatic chain is sufficiently long. In an analogous manner, β-chloropropionic acid condenses with benzenoid compounds to form ring ketones.


ClCH₂CH₂COOH +
Cl
CO
CH₂
CH₂
Cl
CO
CH₂
CH₂
Cl
+ HCl + H₂O

A similar ring synthesis is the preparation of 1,6-dihydroxypyrene from 2, 2′-(diacetylchloride)-biphenyl, *i.e.*, xenene-2, 2′-diacetyl chloride

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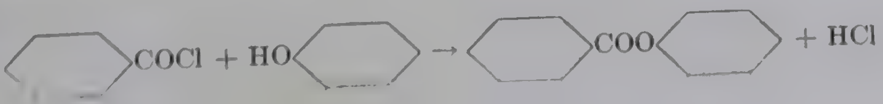
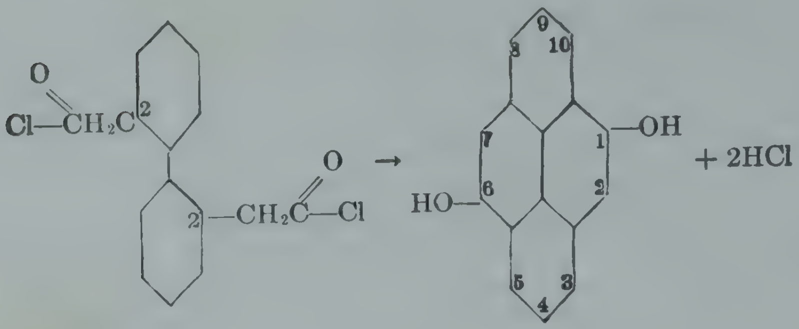
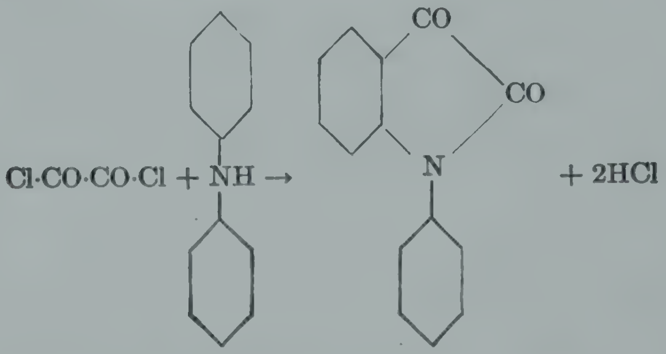
* NEWTON and GROGGINS, *Ind. Eng. Chem.*, **27**, 1397 (1935).

When benzoyl chloride is condensed with phenol at low temperatures, an esterification occurs and a 94 per cent yield of phenyl benzoate is obtained. U. S. 2,345,006 (1944).

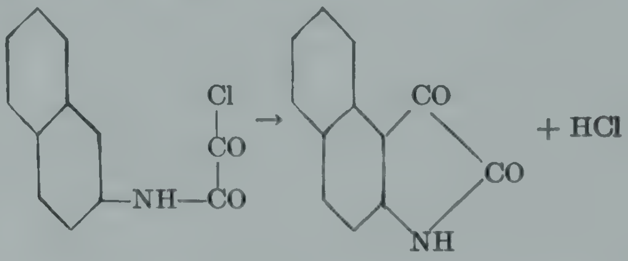

COCl + HO
→
COO
+ HCl



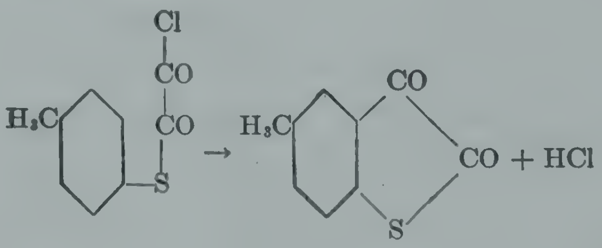
Ring Diketones.—In this class are included the isatins, thioisatins and acenaphthenequinones. Isatins in which the N is substituted may be prepared by condensing secondary amines and oxalyl chloride:[1]



When aryloxamic acid chlorides are treated with aluminum chloride, isatins in which the N is not substituted are obtained:



Thioisatins are obtained from thioaryloxalic acid chloride, according to a method developed by Stollé:



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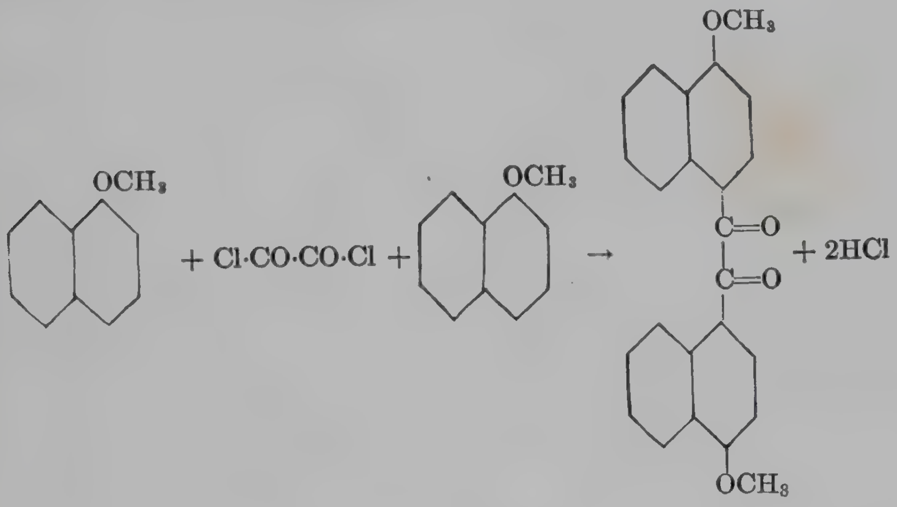
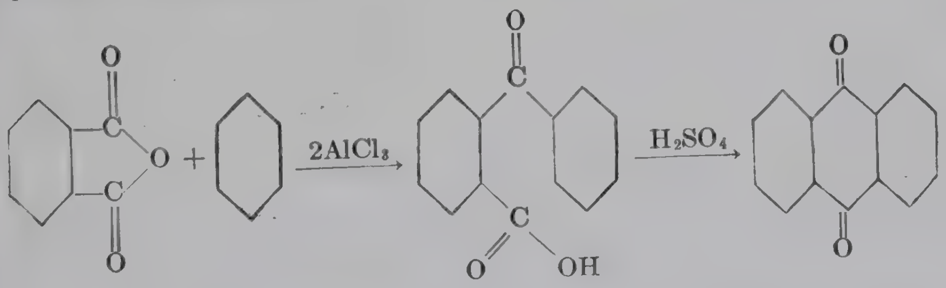
[1] Stollé, Ger. 281,046 (1913).

Open Diketones.—When ethers of aromatic hydrocarbons are condensed with oxalyl chloride in the presence of anhydrous aluminum chloride, open diketones are formed. In many reactions, oxalyl chloride reacts similarly to phosgene. The formation of 4, 4′-dimethoxybinaphthoyl by this method is shown below.



Phenylamidooxalyl chloride ($C_6H_5NH{\cdot}COCOCl$) does not react so readily as oxalyl chloride. The former does not react with benzene but does react with anisoles and other phenol ethers to form diketones.

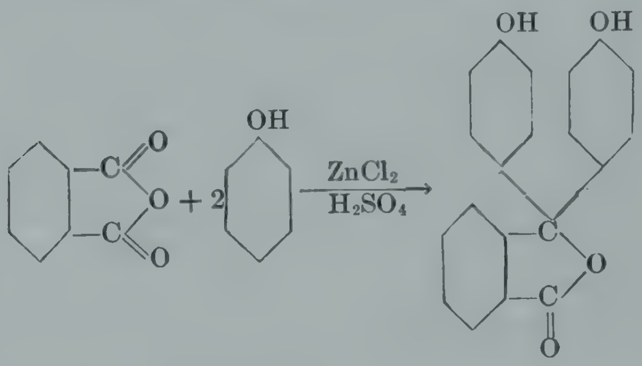
Keto Acids.—The preparation of keto acids is among the most important industrially of the numerous syntheses made possible by the Friedel-Crafts reaction. The benzoylbenzoic acids, which are obtained by condensing phthalic anhydride with aromatic compounds, can readily be converted to anthraquinone derivatives by simple dehydration with sulfuric acid. The steps involved in the synthesis of anthraquinone may be represented as follows:



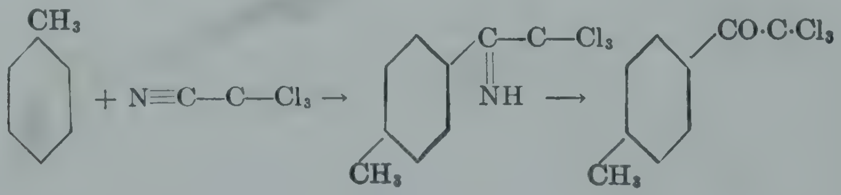
Because of the importance of keto acids to the vat-dye industry, the theoretical and technical aspects of this synthesis will be discussed in some detail later in this chapter. When substituted benzenoid compounds (except nitro derivatives) are used, it is feasible to obtain analogous anthraquinone derivatives as end products. Similar syntheses may be made employing substituted phthalic anhydride (including nitro derivatives) as one of the reactants.

When hydroxy compounds are condensed with phthalic anhydride, it is possible, when employing elevated temperatures, to proceed directly to the hydroxyanthraquinone derivatives. Hystazarin[1] is thus prepared by treating pyrocatechol in the presence of an excess of phthalic anhydride. For the production of quinizarin, hydroquinone is used, and the double salt sodium-aluminum chloride is advantageously employed. Gubelmann has shown that it is feasible to use concentrated sulfuric acid instead of aluminum chloride in condensing 3, 4-dichlorophenol with phthalic anhydride to prepare 2- (or 3-) chloro-1, 4-dihydroxyanthraquinone.[2]

When phenols are condensed in inert solvents with phthalic anhydride under comparatively mild conditions, it is possible to obtain the hydroxy keto acid in substantially good yields. The condensation of phthalic anhydride and phenol at 120°C. in the presence of zinc chloride leads almost exclusively to phenolphthalein. The reaction is accelerated by the addition of relatively small quantities of concentrated sulfuric acid.[3]



Ketimides.—Houben and Fischer have shown that acid nitriles react with phenols and phenol ethers in the presence of aluminum chloride.[4] Hydrocarbons can also be condensed when the very active trichloroacetonitrile is used, and the formation of ω-trichloromethyl *p*-tolyl ketone may be represented as follows:



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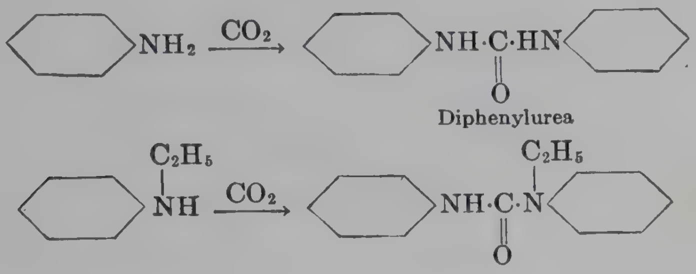
[1] Ger. 298,345 (1914).

[2] Gubelmann, U. S. 1,655,863 (1928).

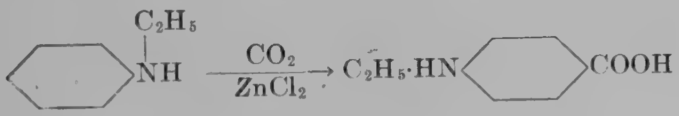
[3] Hubacher, U. S. 1,940,494 (1933).

[4] HOUBEN and FISCHER, *J. prakt. Chem.* [2], **123**, 89, 262, 313 (1929).

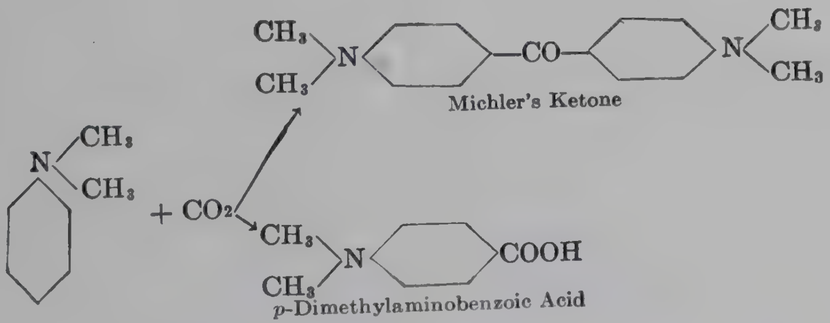
Ureas.—When carbon dioxide is condensed with amines in the presence of aluminum chloride, ureas and alkylaminobenzophenones are obtained.


NH₂
CO₂
NH·C·HN
O
Diphenylurea
C₂H₅
NH
CO₂
NH·C·N
C₂H₅
O

When mild conditions of temperature and a weaker catalyst such as zinc chloride are used, the secondary amines yield alkylamino carboxylic acids.

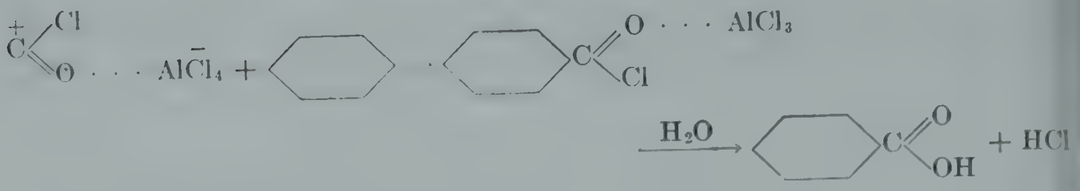

C₂H₅
NH
CO₂
ZnCl₂
C₂H₅·HN
COOH

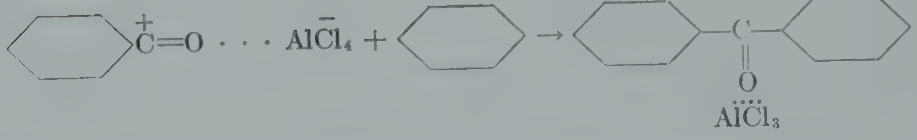
Similarly, the reaction of tertiary amines with carbon dioxide may be adjusted to lead to the formation of aromatic ketones and amino aromatic carboxylic acids, thus:


CH₃
CH₃
N
—CO—
N
CH₃
CH₃
Michler's Ketone
N
CH₃
CH₃
+ CO₂
CH₃
N
CH₃
COOH
p-Dimethylaminobenzoic Acid

CARBOXYLIC ACID DERIVATIVES

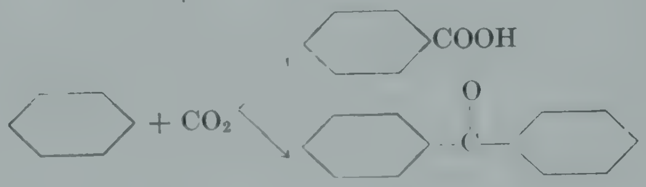
By Action of Phosgene.—Although phosgene reacts directly with many organic compounds, its action on aromatic compounds is facilitated by Friedel-Crafts catalysts. In the hypothetical organo-aluminum chloride addition compound, both chlorine atoms can presumably be activated. Phosgene can accordingly condense with benzene to yield benzoyl chloride (which may be hydrolyzed to benzoic acid) and benzophenone. A longer reaction time and more drastic conditions favor replacement of the two chlorine atoms by phenyl nuclei.



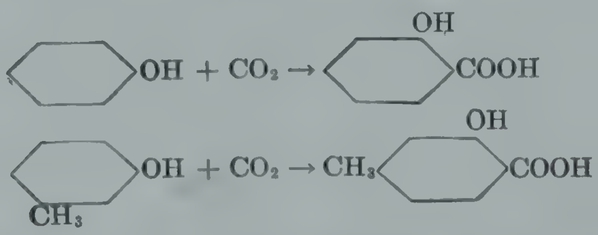


Norris and Fuller have shown that the further action of the aluminum chloride complex of benzoyl chloride could be inhibited by using carbon disulfide—in which the addition compound is sparsely soluble—as a solvent.[1] The yield of benzoic acid can also be increased to 85 to 90 per cent by operating at low temperatures, which diminishes the solubility and therefore the activity of the $C_6H_5{\cdot}COCl \cdots AlCl_3$ complex.

By Direct Action of CO_2 and CO.—Carboxylic acids can be prepared by the direct reaction of carbon dioxide with benzene and chlorobenzene in the presence of aluminum chloride.[2]



When phenols are treated with CO_2 under a pressure of 50 atmos., several products may be obtained, depending on the proportions of reactants used and the temperature employed. The formation of salicylic acid and of *m*-cresotic acid may be represented as follows:



When the ratio of $AlCl_3$ to phenol is increased, 4, 4′-dihydroxybenzophenone is the principal product.[3] An increased yield of carboxylic acid is favored by lower temperatures and the substitution of a milder condensing agent such as zinc chloride. *p*-Ethylaminobenzoic acid and

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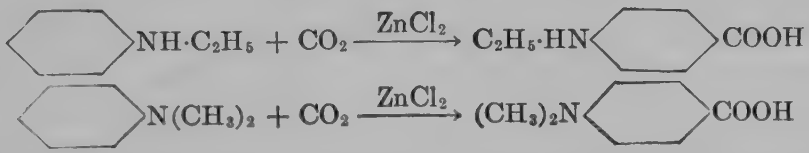
[1] U. S. 1,542,264.

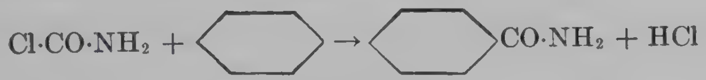
[2] Brit. 307.223 (1929).

[3] Brit. 353,464 (1931).

-dimethylaminobenzoic acid can be obtained by condensing the requisite lkylaniline with CO_2 in the presence of zinc chloride:



Amides are obtained by condensing carbamyl chloride with hydro-arbons according to the following reaction:

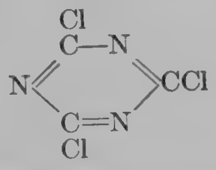


Carbon monoxide in the presence of boron trifluroride reacts with lcohols to yield carboxylic acids. At about 250°C. and 900 atmos. ressure, the following reactions take place:[1]

$$CH_3OH + CO \xrightarrow{BF_3} CH_3COOH$$
$$C_2H_5OH + CO \xrightarrow{BF_3} CH_3CH_2COOH$$

From—Cyaphenines.—When benzene or its homologues are treated with cyanuric chloride in the presence of aluminum chloride, cyaphenine or its homologues are obtained. When cyaphenine is hydrolyzed with sulfuric acid, benzoic acid is produced. The reactions involved are as follows:

$$3CNCl \rightarrow (CNCl)_3 \tag{1}$$

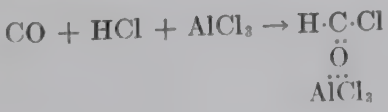


$$(CNCl)_3 + 3AlCl_3 + 3C_6H_6 \rightarrow (C_6H_5CN)_3{\cdot}3AlCl_3 + 3HCl \tag{2}$$
$$(C_6H_5CN)_3{\cdot}3AlCl_3 + 6H_2O \rightarrow 3C_6H_5COOH + 3AlCl_3 + 3NH_3 \tag{3}$$

The ammonia formed in reaction (3) will, of course, combine with the excess of sulfuric acid present in the hydrolysis.

ALDEHYDE SYNTHESES

The utility of carbon monoxide as a condensing agent to form aromatic aldehydes is, in all probability, dependent on the initial formation of the hypothetical $AlCl_3$ addition compound of formyl chloride.



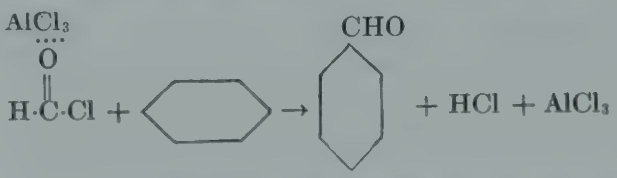
$$CO + HCl + AlCl_3 \rightarrow \underset{\substack{\ddot{O}\\ \ddot{A}lCl_3}}{H{\cdot}C{\cdot}Cl}$$

---

[1] Loder, U. S. 2,253,525 (1941).

Hydrogen chloride is needed for the formation of this active complex which, evidently, reacts similarly to acyl chlorides.

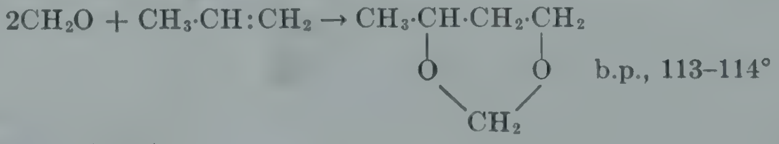
Aldehydes may be made by reacting carbon monoxide with aromatic hydrocarbons or their substitution products under 1,200 lb. pressure in the presence of aluminum chloride.[1,2,3] The reaction proceeds very slowly at first but, once under way, the velocity increases progressively. Hydrogen chloride or a limited amount of water, which causes the liberation of HCl, has been found a useful agent in initiating the reaction, thus shortening the long and costly induction period. More recently, it has been found satisfactory to leave a residue of aldehyde-aluminum chloride complex in the autoclave into which fresh reactants are then added. This stratagem is instrumental in cutting down the induction period from 10 to 3.5 hr.[4] Another technic achieving this end is to prepare an addition compound of formyl chloride by causing carbon monoxide to react with hydrogen chloride in the presence of aluminum chloride and copper under 130 atmos. pressure at 50°C. The addition complex, which is unstable in the presence of moisture, may of course be employed for the preparation of aromatic aldehydes.[5]



When aromatic nitro compounds are used as solvents, the preceding aldehyde synthesis can be made to take place at 60°C. without the use of pressure.[6]

SYNTHESIS OF FORMALS

Not only are aldehydes prepared by the Friedel-Crafts reaction, but the pertinent metal halides also catalyze reactions involving their use. Thus, formals (4-methyl meta-dioxanes) can be made by condensing formaldehyde with propylene in the presence of boron trifluoride associated with water in a ratio of 1:1 to 5. The reaction leading to the formation of butylene glycol cyclic formal is as follows:[7]



$$2CH_2O + CH_3{\cdot}CH{:}CH_2 \rightarrow CH_3{\cdot}\underset{\substack{|\\O\diagdown}}{CH}{\cdot}CH_2{\cdot}\underset{\substack{|\\\diagup O}}{CH_2} \quad \text{b.p., 113–114°}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2$$

---

[1] Ger. 281,212 (1914).

[2] Brit. 3,152 (1915).

[3] Holloway and Krase, *Ind. Eng. Chem.*, **25**, 497 (1933).

[4] Larson, U. S. 1,989,700 (1935).

[5] U. S. 1,976,682 (1934).

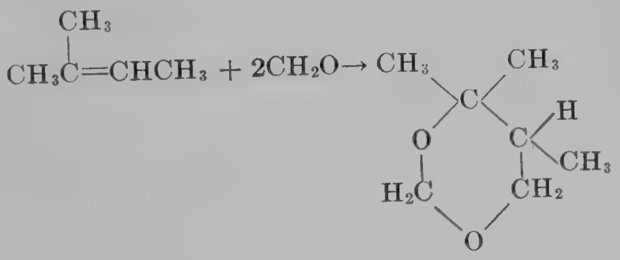
[6] Ger. 403,489 (1924).

[7] Loder, U. S. 2,289,548 (1942).

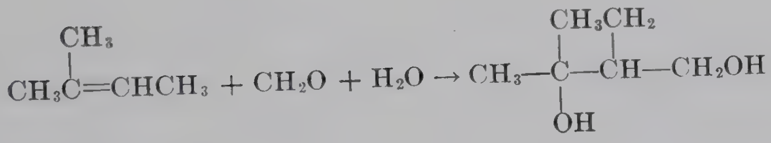
Higher boiling formals (b.p. up to 250°) are always obtained, but the yield of lower boiling formals is almost four times as large as the higher boiling derivatives.

According to Rosen, a BF_3—H_2O catalyst of a concentration of 1:1 to 5 is too potent for the reaction of tertiary unsaturated olefins with aldehydes.[1] The reaction is so rapid as to be uncontrollable and results in the formation of products having a wide boiling range. When at least 9 moles of water are associated per mole of boron trifluoride, such a catalyst is useful for reactions such as between formaldehyde and isobutylene. The condensation is carried out in an autoclave and is initiated at room temperature. Owing to the exothermic reaction, the temperature rises rapidly. The products are 4, 4-dimethyl-meta-dioxane and 3-methyl-1, 3-butanediol.

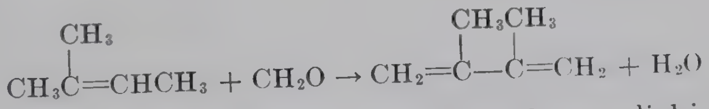
The reactions of formaldehyde with trimethylethylene lead to 3, 4, 4-trimethyl-meta-dioxane, 2, 3-dimethyl-1, 3-butanediol, and 2, 3-dimethylbutadiene-1, 3 as follows:



(1)



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_3 + CH_2O + H_2O \rightarrow CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_2}{\overset{|}{C}}H-CH_2OH \qquad (2)$$



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_3 + CH_2O \rightarrow CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2 + H_2O \qquad (3)$$

The conversion of the dimethyl-meta-dioxane to the butanediol is preferably accomplished by halohydrolysis, *i.e.*, by chlorine in aqueous solution.[2] Upon dehydration, the diol is converted to 2, 3-dimethylbutadiene-1, 3.

SYNTHESIS OF ARYLALKANOLS

The synthesis of β-phenylethyl alcohol, which is an important constituent of rose oil and many blended perfumes, has attracted many investigators.[3,4,5,6] When ethylene oxide and benzene are condensed in

[1] Rosen and Arundale, U. S. 2,368,494 (1945).

[2] U. S. 2,367,324 (1945).

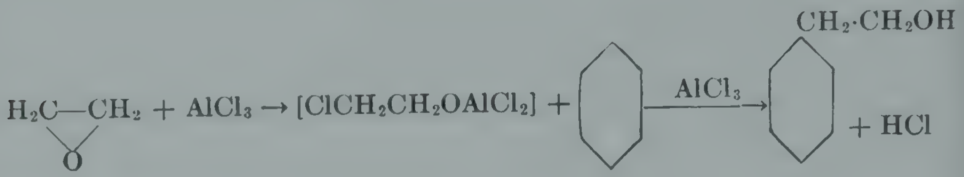
[3] Valik and Valik, U. S. 1,944,959 (1934).

[4] Carpenter, U. S. 2,013,710 (1935).

[5] Hopff, U. S. 2,029,618 (1936).

[6] Klipstein, Can. 340,555 (1934).

the presence of aluminum chloride, β-phenylethyl alcohol is obtained. Tolyl and xylyl derivatives, as well as propanol derivatives, can, of course, be prepared in a similar manner.



The preceding suggested mechanism of reaction indicates that 1 mole $AlCl_3$ is required for the formation of an addition complex after the oxide ring is broken. An excess over this amount is presumably required to effect the normal condensation of the alkyl halide with benzene. In practice, it has been found desirable to use about 1.5 moles $AlCl_3$ per mole of ethylene oxide so that the reaction can be carried out at the lowest practical temperature. The removal of the liberated hydrogen chloride by passing a current of air through the reactor has been found instrumental in inhibiting the formation of undesirable by-products. It has also been suggested that the alkylene oxide be separately dissolved in benzene and then run into a suspension of cooled aluminum chloride in benzene at 0 to 10°C.,[1] for temperature control is an important factor in obtaining good results.

Propylene and isobutylene oxides can be substituted for ethylene oxide in the preceding syntheses. Similarly numerous aromatic compounds such as toluene, chlorobenzene, anisole, as well as cycloparaffins, can replace benzene.

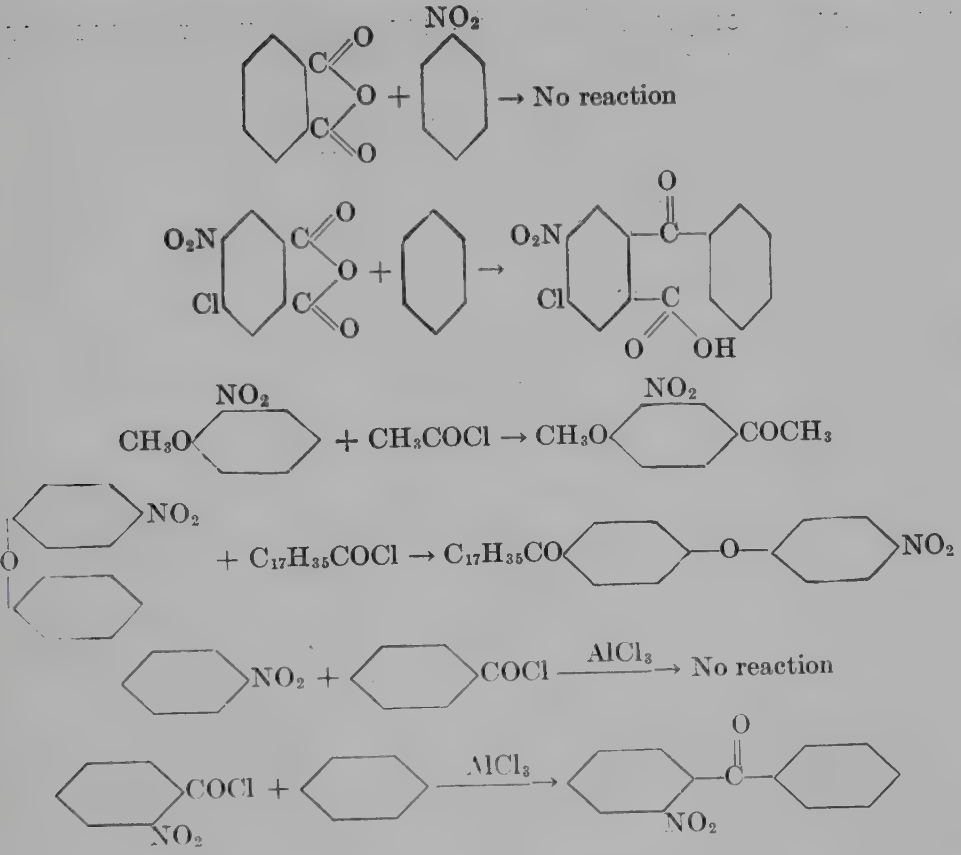
From an inspection of the $AlCl_3$—ethylene oxide addition compound, it can be predicted that small quantities of impurities such as β-phenylethyl chloride, dibenzyl, and ethylene chlorohydrin will be formed as a result of side reactions.

REACTIONS OF NITRO COMPOUNDS

Nitrobenzene does not enter into normal Friedel-Crafts syntheses. When subjected to reaction with an alkylating agent such as isopropyl bromide, reduction of the nitro group and halogenation of the benzene nucleus occur, and a slight conversion of nitrobenzene to *o*- and *p*-chloroanilines occurs. If, however, the aromatic nucleus contains a highly activating substituent in addition to the nitro group, then normal reactions become possible.

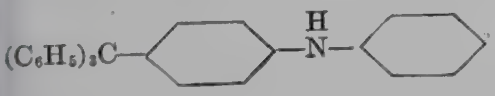
---

[1] Theimer, U. S. 2,047,396 (1936).

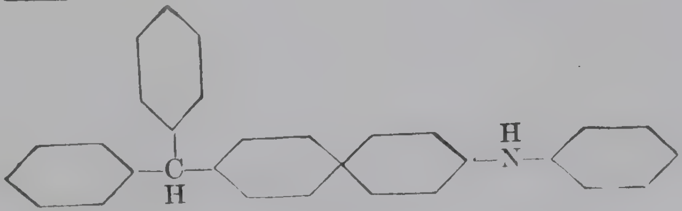

NO2
No reaction
O2N
Cl
OH
CH3O
+ CH3COCl
COCH3
+ C17H35COCl
C17H35CO
COCl
AlCl3
No reaction
AlCl3

PREPARATION OF PRIMARY AND SECONDARY AMINES

Secondary aromatic amines enter into reaction with highly reactive substances of the *tert*-butyl chloride type to yield biphenyl derivatives which are useful in rubber compounding. The reaction products of diphenylamine with triphenylmethyl chloride are *p*-phenylaminotetraphenylmethane and 4-diphenylmethyl-4′-phenylaminobiphenyl:[1]



and



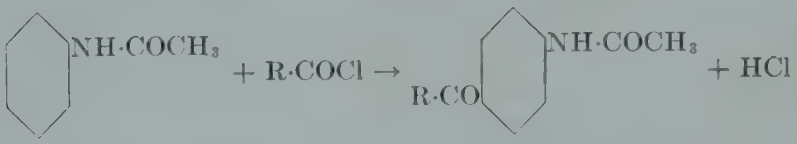
In a similar manner, *p-tert*-butylaniline can be prepared by reacting molar equivalents of *tert*-butyl chloride and acetanilide.[2] The acetanilide is suspended in ethylene dichloride containing molar proportions of aluminum chloride, and the mixture is cooled to −10°C. *tert*-Butyl chloride is then added slowly, the temperature being maintained at −5°C. If the reaction complex is decomposed with water and the solvent removed with steam, *p-tert*-butylacetanilide is obtained as a crystalline mass. The primary amine is obtained by hydrolysis of the anilide with alkali or acid.

---

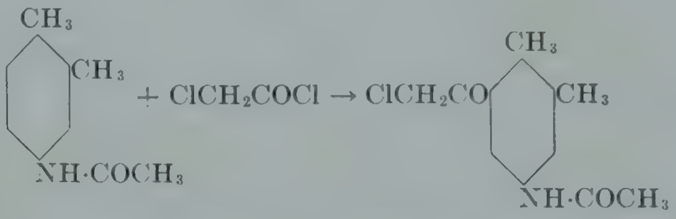
[1] Campbell, U. S. 1,950,079 (1934).

[2] Herstein, U. S. 2,092,973 (1937).

The anilides readily undergo acylation in the presence of aluminum chloride and a solvent. Thus, acetanilide and acyl halides react in accordance with the following general equation.



Alkylated acetanilides undergo reaction with chloroacetyl chloride in a similar manner.



PREPARATION OF HALOGENO COMPOUNDS

1. Haloparaffins.—When ethylene, propylene, and similar olefins react with hydrogen chloride in the presence of aluminum chloride, the corresponding alkyl halide is formed, thus:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3{\cdot}CH_2Cl$$

If these olefins are used in alkylation reactions, they combine with the liberated hydrogen chloride and are transformed into the reactive alkyl halides. The presence of some hydrogen chloride initially tends to accelerate the rate of reaction and to increase the yield of alkylated compound.

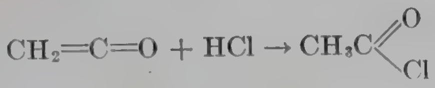
Saturated aliphatic hydrocarbons can also be chlorinated in the presence of aluminum chloride. Polychlorinated ethane[1] and hexane[2] have thus been obtained. When chlorine and ethylene dichloride in a ratio of about 0.55 to 0.75 chlorine per part ethylene dichloride are passed into molten KCl-$AlCl_3$ at 350°C., a 64 per cent yield of 1, 1, 2-trichloroethane is obtained.[1]

---

[1] U. S. 2,034,292 (1935).

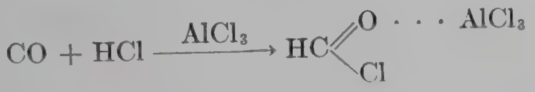
[2] Brit. 286,726 (1928).

2. **Acid Chlorides.**—Carboxylic acid anhydrides behave similarly to olefins and form acid chlorides. Thus, ketene yields acetyl chloride



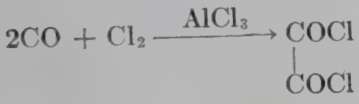
$$CH_2{=}C{=}O + HCl \rightarrow CH_3C\begin{matrix}\nearrow O\\ \searrow Cl\end{matrix}$$

Carbon monoxide and hydrogen chloride form a formyl chloride complex with aluminum chloride, whereas carbon monoxide and chlorine yield oxalyl chloride at 200°C.[2]



$$CO + HCl \xrightarrow{AlCl_3} HC\begin{matrix}\nearrow O \cdots AlCl_3\\ \searrow Cl\end{matrix}$$

50°C. and 1,200 lb. pressure

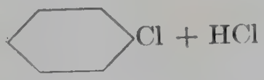


$$2CO + Cl_2 \xrightarrow{AlCl_3} \begin{array}{c}COCl\\ |\\ COCl\end{array}$$

200°C. and 200 lb. pressure

3. **Aromatic Halogeno Compounds.**—The customary chlorination of benzene, naphthalene, phenol, etc., in the presence of ferric or aluminum chloride is generally classified as a halogenating process. Mention only is made here for the purpose of showing the relationship between these two unit processes and indicating that the addition of chlorine rather than its removal is the dominant action. This may be due to the following reaction:

$$Cl_2 + AlCl_3 \rightarrow [Al\overset{-}{Cl}_4 \cdots \overset{+}{Cl}] \xrightarrow{C_6H_6}$$



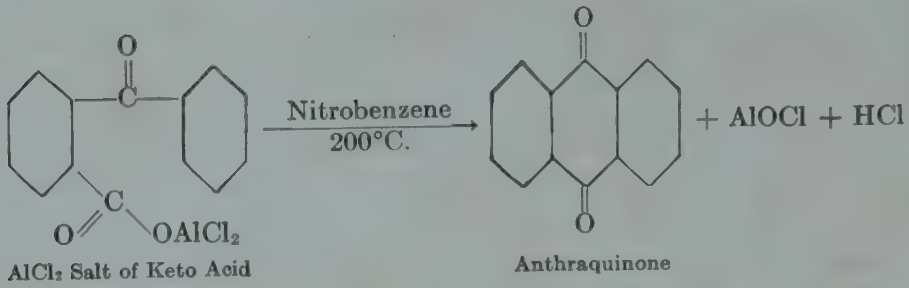
Whether or not the H of the ring is activated by the positively charged chlorine in accordance with the postulates regarding the activating influence of positively charged ions is not known.

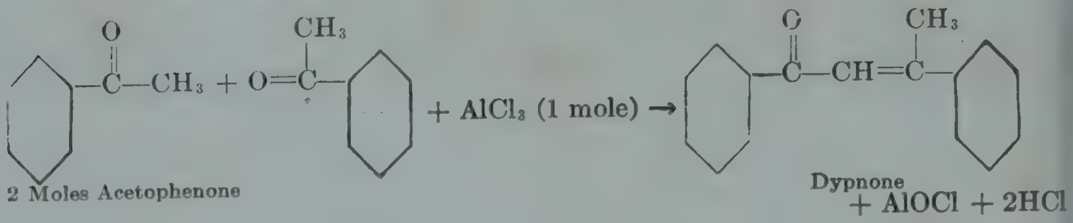
DEHYDRATION REACTIONS

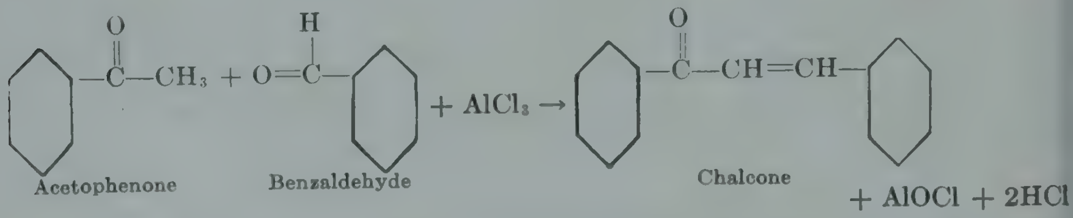
A number of syntheses are made possible through the dehydrating action of aluminum chloride. Although such syntheses involve the removal of the elements of water from 1 or 2 molecules of organic compound, hydrogen chloride is always liberated as the volatile product of reaction. The preparation of anthraquinone, dypnone, and chalcone by this procedure may be represented as follows:

---

[1] U. S. 2,140,549 (1938).
[2] U. S. 2,055,617 (1936).


Nitrobenzene
200°C.
+ AlOCl + HCl
AlCl₂ Salt of Keto Acid
Anthraquinone


+ AlCl₃ (1 mole) →
2 Moles Acetophenone
Dypnone
+ AlOCl + 2HCl


+ AlCl₃ →
Acetophenone
Benzaldehyde
Chalcone
+ AlOCl + 2HCl

Ordinarily, sulfuric acid is employed for the cyclization of keto acids to anthraquinone derivatives, but, when the use of this dehydrating acid leads to a sulfonation product, aluminum chloride may sometimes be used. Thus, when 4′-phenyl-2-benzoylbenzoic acid, which with sulfuric acid undergoes sulfonation before cyclization, is treated in nitrobenzene solution with aluminum chloride, phenylanthraquinone is obtained.[1] In a similar manner, the aluminum chloride salts of many keto acids can be converted to the corresponding anthraquinones. This procedure is not employed industrially, however, because of the low cost of cyclization with sulfuric acid and the purer product thus obtained.

Calloway has shown that dypnone can be obtained with yields of 73 per cent when 2 moles of acetophenone are condensed with the loss of water through the action of 1 mole of aluminum chloride.[2] The reaction is carried out at room temperature using carbon disulfide as a solvent. Similarly, a yield of 91 per cent chalcone, *i.e.*, benzylidene acetophenone, is obtained when molar proportions of acetophenone and benzaldehyde are reacted with 1 mole of aluminum chloride at room temperature for a period of 4 days.

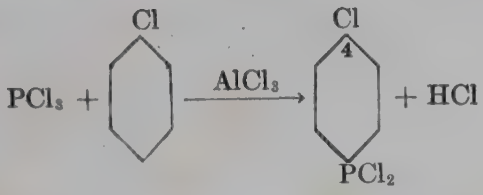
THE SYNTHESIS OF HYDROCARBON DERIVATIVES CONTAINING PHOSPHORUS, SULFUR, AND ARSENIC

When aromatic compounds such as chlorobenzene and toluene are treated with phosphorus trichloride in the presence of aluminum chloride,

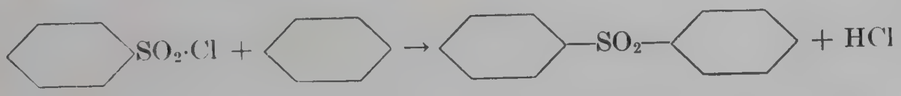
[1] GROGGINS, *Ind. Eng. Chem.*, **22**, 629 (1930).

[2] CALLOWAY, *J. Am. Chem. Soc.*, **59**, 809 (1937).

hosphines are obtained. The preparation of 4-chlorophenyldichlorohosphine is shown below:

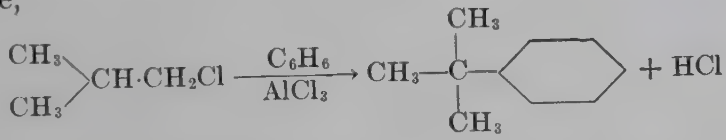


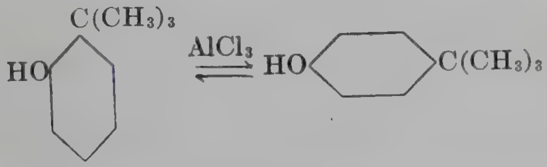
The preparation of diphenylsulfone from benzenesulfonylchloride and benzene is similar to that of diaryl ketones referred to previously.



ISOMERIZATIONS[1]

Previously, it was pointed out that alkylations are equilibrium reactions that are often characterized by position and structural isomerization. For example,

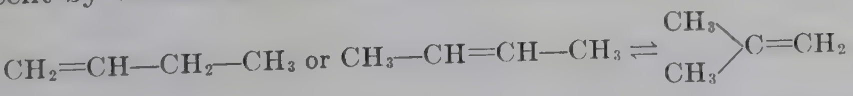




Olefins and Chloroolefins.—To avoid the polymerizing effects of the more active metal halides, zinc chloride and phosphoric acid catalysts have been employed to isomerize olefins and more particularly butene. With a phosphoric acid-diatomaceous earth catalyst at 150°C. and 15 atmos. pressure, butene-1, for example, can be isomerized to butene-2.

$$CH_2{=}CH{-}CH_2CH_3 \rightleftharpoons CH_3{-}CH{=}CH{-}CH_3$$

If the normal butene, in a gaseous state, is brought into contact with the phosphoric acid catalyst at about 300°C. for a contact time of 5 sec. instead of 100 to 200 sec. used in the previous example, approximately 15 per cent by volume is converted to isobutene.[2]



$$CH_2{=}CH{-}CH_2{-}CH_3 \text{ or } CH_3{-}CH{=}CH{-}CH_3 \rightleftharpoons (CH_3)_2C{=}CH_2$$

The chloroolefins obtained by the addition of chlorine to 1,3-butadiene are similarly susceptible to position isomerization in the presence of metal halides.[1] Thus, the less desirable 1, 2-dichlorobutene-3 can be converted to the technically important 1, 4-dichlorobutene-2 by treatment with about 5 per cent by weight of a comminuted mixture of $AlCl_3—FeCl_3$.

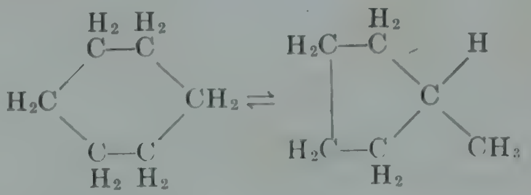
---

[1] Only a few examples of isomerization are given here, since a more comprehensive discussion is beyond the scope of this book.

[2] U. S. 2,220,693 (1940).

$$\underset{32\%\ 1,\ 2\text{-Dichlorobutene-3}}{CH_2Cl\cdot CHCl\cdot CH{:}CH_2} \underset{5°C.}{\overset{5\%\ AlCl_3\cdot FeCl_3}{\rightleftharpoons}} \underset{68\%\ 1,\ 4\text{-Dichorobutene-2}}{CH_2Cl\cdot CH{:}CH\cdot CH_2Cl}$$

Cycloparaffins.—*Methylcyclopentane* and *cyclohexane* enter into reversible isomerizations with only minor side reactions in the presence of aluminum chloride.



Glazebrook and Lovell have shown that the reaction is promoted by HCl or H_2O, and, as in similar isomerizations, the equilibrium mixture is determined by the temperature.[2] The methyl cyclopentane content at various temperatures is as follows:

25°, 12.5%	45°, 16.2%	65°, 21.4%
35°, 14.5%	55°, 19.2%	77.4°, 25.6%

The transformation of cyclohexane into methylcyclopentane is effected in spite of the fact that the strain-free cyclohexane ring is more stable and less reactive. The need for hydrogen chloride as a coreactant suggests the formation of the highly active $\overset{+}{H} \cdots \overset{-}{AlCl_4}$ addition complex as a precursor to isomerization.

Isomerization of Paraffins.[3]—When alkanes containing four or more carbons are treated with metal halides and hydrogen chloride under relatively mild conditions, isomerization to branched-chain paraffins occurs. The reaction is reversible and is accompanied by some cracking, dehydrogenation, and polymerization of the resulting olefins. The data pertaining to equilibrium products of butane, pentane, and hexane at specific temperatures are presented in Table I, below.[4]

---

[1] U. S. 2,242,084.

[2] GLAZEBROOK and LOVELL, *J. Am. Chem. Soc.*, **61,** 1717 (1939).

[3] For a review of the isomerization of paraffins (as well as of other hydrocarbons) see EGLOFF, HULLA, and KOMAREWSKY, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, 1942.

[4] EVERING, FRAGEN, and WEEMS, *Chem. Eng. New*, **22,** 1889 (1944); see also PINES and coworkers, *J. Am. Chem. Soc.*, **67,** 631, (1945).

'ABLE I.—EQUILIBRIUM DISTRIBUTION OF BUTANES, PENTANES, AND HEXANES

	Liquid volume, %			
	21°	100°	150°	204°
utanes:				
Isobutane	85	75	65	57
n-Butane	15	25	35	43
entanes:				
Isopentane	95	85	78	71
n-Pentane	5	15	22	29
exanes:				
Neohexane	57	38	28	21
2, 3-Dimethylbutane	11	10	9	9
2-Methylpentane	20	28	34	36
3-Methylpentane	8	13	15	17
n-Hexane	4	11	14	17

Although the phenomenon of isomerization of alkyl groups incidental o alkylation reactions has long been known, the isomerization of the lkanes is a comparatively recent development. In 1935, Moldavskii nd coworkers reported on the conversion of hexane with aluminum hloride fortified by hydrogen chloride or alkyl halides.[1] Glazebrook nd coworkers found that yields of 55.9 per cent of 2-methylbutane could e obtained by treating pentane in the liquid phase with aluminum hloride and hydrogen chloride.[2] Ipatieff and Pines reported that -butane could similarly be converted principally to isobutane by carrying ut the reaction at approximately 200°C. and 40 atmos. pressure.[3]

On account of the technical importance of isobutane and the higher ranched-chain paraffins in the production of high-octane motor fuels,[4] he isomerization of normal paraffins has received intensive study, and umerous patents have been obtained during the past few years. These over (1) diverse metal halides and combinations thereof,[5] (2) continuous operating conditions and the use of fluid or molten catalysts,[1] (3) conse vation and recovery of catalysts,[2] and (4) design of operating equipmen

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[1] MOLDOWSKII, KOBUIL'SKAYA, and LIVSHITZ, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 1791 1935).

[2] GLAZEBROOK, PHILLIPS, and LOVELL, *J. Am. Chem. Soc.*, **58**, 1944 (1936).

[3] U. S. 2,169,494 (1939); Brit. 498,463 (1938).

[4] It is appropriate to observe that this isomerization reaction had far-reaching vartime effects by limiting allocations of butanes to the synthetic rubber program, ecessitating greater use of grain alcohol for preparation of butadiene. This esulted in a diminution of 150 million bushels of feed for livestock annually—thereore less meat.

[5] U. S. 2,169,494 (1939); 2,250,118 (1941); 2,265,548 (1941); 2,266,011 (1941); ,290,189 (1942); 2,300,160 (1942); 2,316,247 (1943); 2,316,248 (1943); 2,327,188 1943); 2,327,593 (1943); 2,332,275 (1943).

POLYMERIZATION

Friedel and Crafts recognized that metal halides could be used n only as condensing catalysts but also as effective polymerizing agent They noted the formation of a brittle resin by the autocondensation benzyl chloride.

$$C_6H_5CH_2Cl \rightarrow C_6H_5CH_2{\cdot}C_6H_4CH_2Cl \rightarrow C_6H_5CH_2(C_6H_4CH_2)_nC_6H_4CH_2Cl$$

Aralkyl halides or reactants such as haloolefins and aromatic hydroca bons which condense to produce aralkyl halides or arylated olefins poly merize with the evolution of hydrogen chloride and yield relativel low-molecular-weight linear polymers.

Sparks and coworkers have improved the well-known art of poly merizing alkyl and aralkyl halides by carrying out the Friedel-Craft reaction at low temperatures in the presence of a solvent.[4] When benzy chloride, dissolved in liquid propane (b.p., −45°C.), is treated with an equa volume of ethyl chloride containing 1 per cent by weight of aluminun chloride, rapid polymerization with the evolution of hydrogen chlorid occurs. The reaction mass, after washing with ethanol to remov aluminum chloride and benzyl chloride, is dried at 105°C. A clear, hard slightly yellow resin which is brittle at room temperatures is obtained.

Olefins, chloroolefins, and diolefins, which in the presence of hydroge chloride and metal halide form saturated and unsaturated alkyl halides are readily susceptible to polymerization and copolymerization. Thus, isobutylene in a suitable solvent, such as liquid ethylene, is polymerized by aluminum chloride or boron trifluoride at a temperature of −80°C. or lower, and relatively high-molecular-weight (100 to 1,000 units) polymers are obtained. Since there is only one double bond available in isobutylene and other simple olefins, the resultant polymers are practically saturated and do not readily enter into secondary reactions. When, however, isobutylene, dissolved in-liquid ethylene, is copolymerized with 2, 3-dimethylbutadiene-1, 3 at −90°C. in the presence of methyl chloride, high-molecular-weight (molecular weight, 110,000), unsaturated polymers are obtained.[5] Such long-chain interpolymers which can form cross inkages are used in the manufacture of "Butyl" rubbers. The reaction nay be represented as follows:

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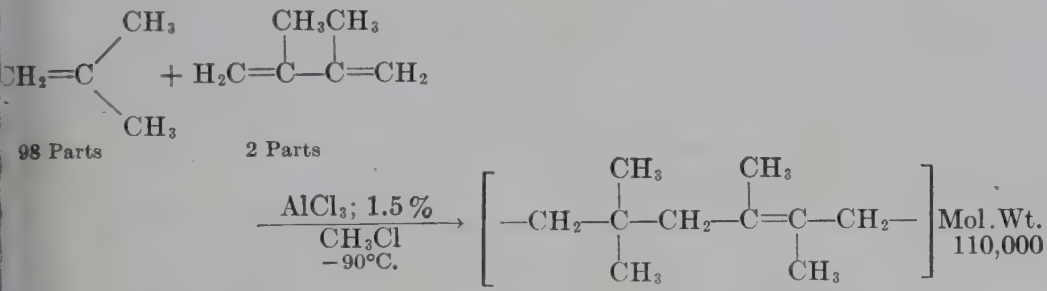
[1] U. S. 2,249,366 (1941); 2,257,896 (1941); 2,283,143 (1942); 2,288,477 (1942); 2,291,376 (1942); 2,300,235 (1942); 2,348,700 (1944); 2,370,118 (1945).

[2] U. S. 2,307,053 (1943); 2,331,429 (1943).

[3] U. S. 2,360,699 (1944); 2,360,700 (1944); 2,365,917 (1944); 2,366,117 (1944); 2,366,628 (1944).

[4] Sparks and Field, U. S. 2,241,488 (1941).

[5] U. S. 2,356,130 (1944).



Unsaturated fatty acids and their esters can be polymerized to products that are useful as lubricants or addition agents for lubricants. The nore unsaturated fatty acids yield resins.

Cracked petroleum distillates conforming to rigid specifications egarding boiling range, degree and nature of unsaturation, aromatic ontent, specific gravity, etc., are used for the production of hydrocarbon esins. The poymerization is carried out in vessels equipped for adequate ieat transfer to take care of the exothermic reaction and thus avoid xcessive darkening of the resinous product.

The polymerization products that can be obtained through the intervention of metal halides are legion. Practically every class of compound an be converted to a resin of more or less value.[1]

OTHER REACTIONS CATALYZED BY ALUMINUM CHLORIDE

Previously, it was noted that reactions catalyzed by metal halides may nvolve simple addition, double decomposition, hydrogenation and lehydrogenation, chlorination and dehydrochlorination, polymerization, somerization, dehydration, inter- and intramolecular rearrangements, ission, etc. Many of these phenomena have been observed in the yntheses that have thus far been discussed. In addition to activating r catalyzing such synthetical processes, aluminum chloride has a disruptive influence from which, under drastic conditions, no compounds re immune. Under controlled conditions, this disruptive influence can e utilized advantageously as in the Fries reaction and the Scholl ondensation.

The Disruptive Influence of Aluminum Chloride.—The disruptive ction of aluminum chloride on both aromatic and aliphatic compounds as been shown by numerous investigators. The loosening of atomic onds with the migration of atoms or groups may be represented by the ollowing reactions:

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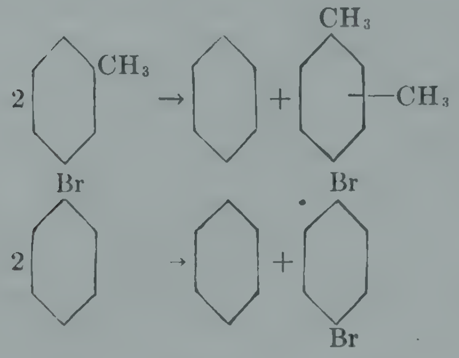
[1] For a more extensive discussion, the reader is referred to THOMAS, "Anhydrous luminum Chloride in Organic Chemistry," *Am. Chem. Soc. Monograph* 87.

$(CH_3)_3C\cdot COCl \rightarrow CO + HCl + C_4H_8$ [BOESEKEN, *Rec. trav. chim.*, **29**, 85 (1910)]



[COPISAROW and LONG, *J. Chem. Soc.*, **119**, 1806 (1921)]

[DUMREICHER, *Ber.*, **15**, 1867 (1882)]

When used in the treatment of lubricating oils and in petroleum cracking processes, aluminum chloride not only functions as a disruptive or fission agent but also exercises a catalytic condensing and polymerizing action. From our knowledge of the composition of crude oils and the nature of the distillates after cracking, it appears that all the above reactions proceed concurrently. Large molecules are labilized and broken down, the fission of the larger nuclei being favored by extreme conditions of temperature and aluminum chloride concentration. Side chains become chlorinated and either form condensation compounds or migrate. The smaller migratory groups then condense or polymerize, forming more stable compounds. The practical application of reactions of these types to the petroleum industry can be summarized as follows.[1]

Decomposition........	Preparation of gasolines by cracking high-boiling hydrocarbons Refining by decomposition of organic compounds of sulfur
Polymerization........	Preparation of lubricants and motor fuels by polymerization of low-boiling hydrocarbons Refining by polymerization of gum-forming constituents
Alkylation............	Preparation of motor fuels by alkylation of paraffins with olefins Synthesis of pour-point depressants by alkylation of aromatics with higher olefins or alkyl halides
Isomerization.........	Preparation of branched paraffins having high antiknock value Ring closure of aliphatic hydrocarbons to confer increased aromaticity

Fries Reaction.[2]—The Fries reaction is the conversion of an ester of a phenol to an acylphenol by means of aluminum chloride:[3]

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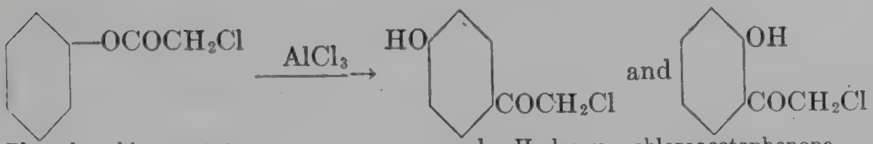
[1] THOMAS, *loc. cit.*

[2] The reader is referred to BLATT, *Chem. Rev.*, **27**, 413–36 (1940); "The Fries Reaction," "Organic Reactions," Vol. I, p. 342, John Wiley & Sons, Inc., New York, 1942, for a more extensive discussion.

[3] FRIES, *Ber.*, **43**, 214 (1910).



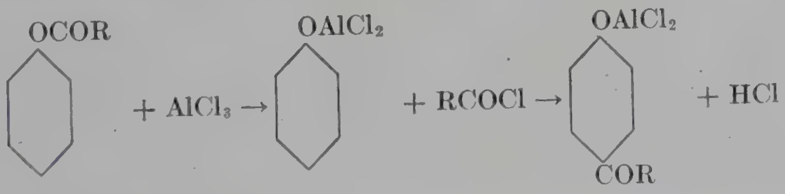
Phenyl-ω-chloroacetate o- and p-Hydroxy-ω-chloroacetophenone

Although the extra step of preparing the ester of the phenol is required, this reaction is usually more satisfactory than the direct acylation of a phenol. Resorcinol, however, can be directly acylated so readily that the Fries reaction would not be chosen.

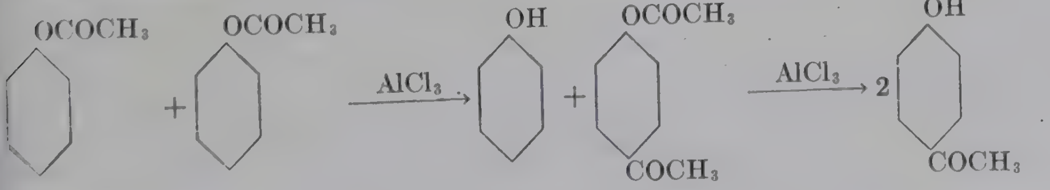
Rosenmund and Schnurr developed the general technic, requiring 1 mole of aluminum chloride per mole of ester of a monohydroxyphenol and leading in many cases, according to the selected conditions, to either the ortho or the para hydroxy ketone.[1] When both of the isomers are formed, they may be separated by differences in volatility with steam, distillation at reduced pressure, solubility characteristics, or ease of extraction with dilute alkali. Excellent yields are obtained in the following representative cases: 4-hydroxybenzophenone,[2] 6-hexoyl-*m*-cresol,[3] and 4-benzoylcatechol[4] from the esters phenyl benzoate, *m*-tolyl hexoate, and catechol dibenzoate, respectively.

Three different mechanisms have been advanced:

1. Aluminum chloride reacts with the phenol ester to form an acid chloride and a phenoxyaluminum chloride, and these two molecules in turn react together:[5]



2. One molecule of the phenol ester acylates another molecule.[6]



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[1] Rosenmund and Schnurr, *Ann.*, **460**, 56–98 (1928).

[2] Rosenmund and Schnurr, *loc. cit.*; Blicke and Weinkauff, *J. Am. Chem. Soc.*, **54**, 330 (1942).

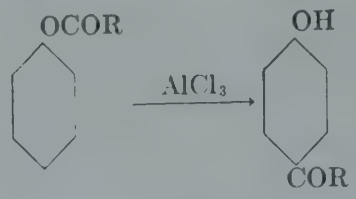
[3] Baltzly and Bass, *J. Am. Chem. Soc.*, **55**, 4292 (1933); Coulthard, Marshall, and Pyman, *J. Chem. Soc.*, **1930**, 280.

[4] Rosenmund and Lohfert, *Ber.*, **61**, 2601 (1928).

[5] Skraup and Poller, *Ber.*, **57**, 2033 (1924); Cox, *J. Am. Chem. Soc.*, **52**, 352 (1930).

[6] Rosenmund and Schnurr, *loc. cit.*

3. A true intermolecular rearrangement occurs.[1]



The first mechanism is similar to an explanation given in this chapter (page 760) for the activity of acetic anhydride (acetyl acetate) in the Friedel-Crafts reaction and, in light of the experimental evidence, appears to be the more acceptable interpretation of the Fries reaction.

Solvent, time, temperature, and the ratio of aluminum chloride influence the reaction and the ratio of the para to the ortho isomer. The presence of a nitro, acyl, or carboxyl group in the phenolic portion of the phenol ester slows up or completely stops the Fries reaction.

The reaction may be carried out in the absence of a solvent or with carbon disulfide as an initial solvent, with subsequent removal and completion of the reaction at higher temperatures. Nitrobenzene, tetrachloroethane, and chlorobenzene are solvents frequently used.

In general, higher reaction temperatures favor the formation of the ortho isomer, and, in a few instances, it has been possible to direct the reaction to the production of but one of the isomers simply by different temperature conditions.[2]

Ralston and coworkers have made a study of the rearrangements of phenyl caprylate at 100°C. in a tetrachloroethane solvent.[3] High aluminum chloride ratios favor para orientation. At an aluminum chloride to phenol ester ratio of 0.5, the para to ortho ratio in the resulting acylphenols is small but increases with time. At 1.1 mole ratio, the para to ortho ratio is small and increases with time, but at 4 hr. is still less than 1. At 1.3 and 2.0 mole ratios, the para to ortho ratio is greater than 1 and remains about the same with increasing time. The ester, the acid chloride, and the ketone form complexes with aluminum chloride; the phenol forms phenoxyaluminum chloride. The formation of the different complexes modifies the effective concentration of aluminum chloride and affects the reaction.

The Scholl Reaction.—Scholl showed that condensations in the aromatic series could be effected whereby intramolecular union of nuclei took place with the splitting off of nuclear hydrogen.[4] The simplest

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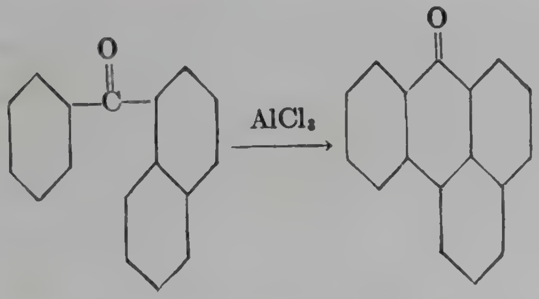
[1] Auwers and Mauss, *Ber.*, **61,** 1495 (1928); *Ann.*, **464,** 293 (1928).

[2] Rosenmund and Schnurr, *loc. cit.*

[3] Ralston, McCorkle, and Segebrecht, *J. Org. Chem.*, **6,** 750 (1941).

[4] Scholl, *Ann.* **394,** 111 (1912); *Ber.*, **43,** 1737 (1910).



example of this reaction is the transformation of α-benzoylnaphthalene into benzanthrone.

It is apparent that the synthesis comprises the preliminary formation of the benzoyl compound according to the Friedel-Crafts reaction, this step being followed by a more drastic treatment with aluminum chloride to effect cyclization. This procedure is of considerable technical importance and finds many applications in the preparation of intermediates for dyes.

CHEMICAL AND PHYSICAL FACTORS

A number of chemical and physical factors have an important bearing on the successful control of the Friedel-Crafts reaction. The most important of these are

1. Quantity of aluminum chloride required.
2. Comparative reactivities, alkylation *vs.* acylation.
3. Effects of other metal halides in aluminum chloride.
4. Effect of size of aluminum chloride particles.
5. Removal or addition of hydrogen chloride.
6. Effect of temperature.
7. Influence of solvents.
8. Hydrolysis of aluminum chloride addition compounds.

Quantity of Aluminum Chloride Required.—The synthesis of hydrocarbons, such as ethylbenzene and its homologues; the isomerization of olefins, paraffins and cycloparaffins; and the polymerization of olefins and alkyl halides lead to the primary formation of unstable aluminum chloride addition compounds which possess no marked unsaturation and which decompose with the formation of the hydrocarbon and the liberation of the aluminum halide. In such reactions, only a relatively small quantity of catalyst (approximately 5 per cent) is required to carry on the reaction.

When alcohols are used as alkylating agents, the quantity of $AlCl_3$ required depends on the type of alcohol. Approximately 0.5, 0.75, and 1.0 mole are needed, respectively, for tertiary, secondary, and primary alcohols.

In the preparation of ketones by condensing acid chlorides, it is necessary to employ 1 mole of $AlCl_3$. The data (Table II) relating to the preparation of benzophenone show the relation between the quantity of catalyst used and the yield of ketone obtained.

TABLE II.—PREPARATION OF BENZOPHENONE. VARIATION OF YIELD WITH AMOUNT OF CATALYST

$$C_6H_5{\cdot}COCl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COC_6H_5$$

Moles $AlCl_3$	Yield	
	Gm.	%
1.5	29.0	93.3
1.3	28.6	92.0
1.1	29.3	94.2
1.0	28.0	90.1
0.9	25.1	80.7
0.8	22.5	72.4
0.6	18.0	57.8
0.4	12.0	38.6
0.2	5.8	18.6
0.0	0.7	2.2

When aliphatic carboxylic acid anhydrides are condensed with aromatic compounds to form alkyl aryl ketones, the use of 2 moles of aluminum chloride results in a yield of approximately 100 per cent based on only one acyl group being reactive. When 3 or more moles of aluminum chloride per mole of anhydride are used, then yields of 75 to 85 per cent based on both acyl groups are obtainable.[1]

TABLE III.—PREPARATION OF ACETOPHENONE FROM ACETIC ANHYDRIDE AND BENZENE

Run No.	Moles $AlCl_3$	Substance added	Yield, %*	M. p.,‡ °C.	Conditions
1	1.1	Control	12	18.2	Time, 5.5 hr.
2	2.3	Control	52 to 53	18.7	Temp., 90°C.
3	2.8	Control	65 to 68	18.8	Benzene, 5 moles
4	3.3	Control	76†	18.8	Acetic anhydride, 1 mole
5	4.4	Control	81 to 82	18.4	
6	3.3	10 gm. Fe	73†	18.8	
7	3.3	5 gm. Al	75 to 77	18.4	
8	3.3	10 gm. $SOCl_2$	57†	19.0	

* Yield per cent, based on both acetyl groups.
† Represents two experiments which check exactly.
‡ The m.p. of acetophenone is 19.6°C.

The relation between the active component, *e.g.*, acid chloride, acid anhydride, or carboxylic acid, and the aluminum chloride may be explained as follows. When an acid chloride, *e.g.*, acetyl chloride, is condensed, the function of the $AlCl_3$ is presumably to labilize the chlorine by adding on to the carbonyl group and forming with it a nonvolatile conducting complex, which may then react with benzene to form the $AlCl_3$ addition compound of acetophenone.[1]

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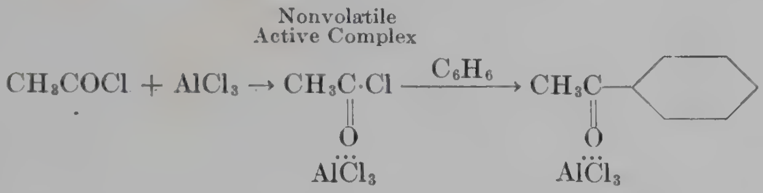
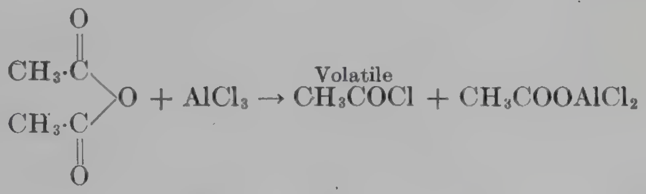
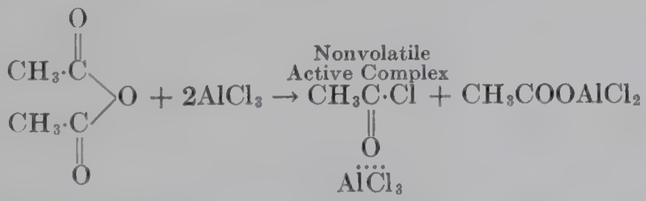
[1] GROGGINS, NAGEL, and STIRTON, *Ind. Eng. Chem.*, **26**, 1313 (1934).


Nonvolatile
Active Complex
CH₃COCl + AlCl₃ → CH₃C·Cl
O
AlCl₃
C₆H₆
CH₃C
O
AlCl₃

When aliphatic or aromatic carboxylic acid anhydrides are similarly condensed, a series of reactions may occur depending on the molar ratio of $AlCl_3$ used. The first mole accomplishes the fission of the acid anhydride with the production of an acid halide and the formation of the aluminum chloride salt of the carboxylic acid. For acetic anhydride, the reactions are probably the following:


O
CH₃·C
O + AlCl₃ → CH₃COCl + CH₃COOAlCl₂
Volatile
CH₃·C
O

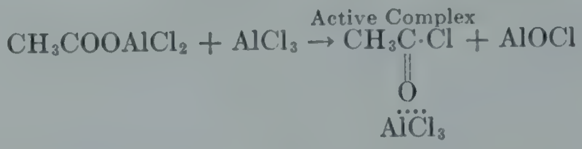
When two molecular proportions of $AlCl_3$ are employed, the acid chloride that is first formed combines with the aluminum chloride to produce the nonvolatile active complex, which in the presence of aromatic compounds reacts to produce alkyl aryl ketones.


O
CH₃·C
O + 2AlCl₃ → CH₃C·Cl + CH₃COOAlCl₂
Nonvolatile
Active Complex
CH₃·C
O
O
AlCl₃

It is apparent from the preceding equations that aluminum chloride acts as a chlorinating agent, and it is also clear that the maximum yields of ketone obtainable with approximately two molecular proportions of AlCl would be about 100 per cent based on one acetyl group and only half as much in terms of both acyl groups. This is confirmed by the data in Table III (page 760). The second acetyl group, which is fixed as the aluminum chloride salt, can also be made to react by adding a third molecular proportion of $AlCl_3$. The reaction is probably as follows:

---

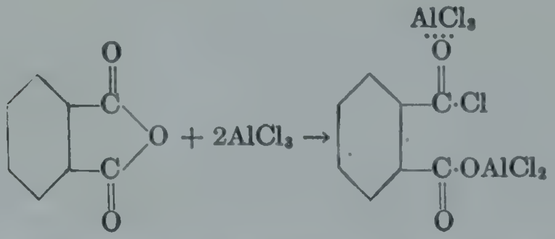
[1] The structure of the conducting, ionized complex may be either $\underset{\overset{\|}{O}}{CH_3\overset{+}{C}} \cdots \overset{-}{AlCl_4}$ or $\underset{\overset{\|}{O}\cdots\overset{-}{AlCl_4}}{CH_3\overset{+}{C}}$, in which the aluminum chloride behaves as an electron acceptor. The second structure, however, depicts the known attachment of $AlCl_3$ to the carbonyl group in a more satisfactory manner. The formation of a mesomeric cation in which the positive charge is distributed between the carbon and oxygen atoms $\left.\begin{matrix} CH_3C \\ \| \\ O \end{matrix}\right\}+$ is also possible.



$$CH_3COOAlCl_2 + AlCl_3 \rightarrow \overset{\text{Active Complex}}{CH_3\underset{\underset{AlCl_3}{\vdots}}{\underset{\|}{\overset{}{C}}\!\!\!\!\!\!\;\;O}\cdot Cl} + AlOCl$$

Further confirmation of this mechanism is presented in Table IV, where it is shown that aliphatic (and aromatic) carboxylic acids react according to the Friedel-Crafts reaction in the presence of at least two molecular proportions of aluminum chloride.[1]

From the preceding discussion of the reaction of aluminum chloride on aliphatic acid anhydrides, it is reasonable to presume that the action of $AlCl_3$ on phthalic anhydride is as follows:



Reactive Acid Chloride Complex

In acylation by the Friedel-Crafts reaction it has always been found advisable to incorporate a slight excess of aluminum chloride to ensure a complete reaction. When the aluminum halide is known to contain inactive or less active constituents, a proportionate allowance is made therefor. Generally, an excess of 5 to 10 per cent over that theoretically required has been found to be productive of the best yields. The limiting conditions will be the purity of the halide and the absence of moisture in the reactants, operating atmosphere, and reaction vessel.

Substitution of Carboxylic Acids for Acid Anhydrides and Acid Chlorides. The discovery that both acyl groups of aliphatic carboxylic acid anhydrides could be made reactive by employing at least three molecular proportions of $AlCl_3$ indicated that many carboxylic acids could be employed for the preparation of alkyl aryl and diaryl ketones. It was subsequently found that acetic, propionic, benzoic, and terephthalic acids, etc., could be employed for making a wide variety of ketones and that the procedure was of wide application and of technical value.[2] The use of a carboxylic acid depends on its conversion to an acid chloride complex, as shown above, and this requires 2 moles of aluminum chloride. The data in Table IV relating to the preparation of *p*-methylacetophenone show that favorable results are obtainable. The yields in similar preparation of 4, 4′-dichlorobenzophenone from chlorobenzoic acid and chlorobenzene are somewhat higher.

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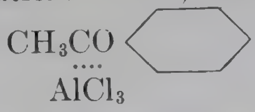
[1] Groggins and Nagel, U. S. 1,966,797 (1934).

[2] Newton and Groggins, *Ind. Eng. Chem.*, **27**, 1397 (1935).

TABLE IV.—PREPARATION OF *p*-METHYLACETOPHENONE FROM ACETIC ACID AND TOLUENE

Expt. No.	Substance added	Moles, $AlCl_3$	Yield, %	Conditions
1	Control	2.0	61.2	Time, 7 hr.
2	2 gm. Al	2.0	67.2	Temp., 100°C.
3	2 gm. Al	2.5	78.7	Moles toluene, 5
4	2 gm. Al	3.0	67.9	Moles acetic acid, 1
5	5 gm. Fe	2.0	66.7	
6	5 gm. Fe	3.0	73.1	

Comparative Reactivities: Acylation and Alkylation.—In the preparation of aryl alkyl ketones, *e.g.*, acetophenone, the $AlCl_3$ is closely bound to the carbonyl of the ketone (before hydrolysis) and is not available for other normal syntheses involving acylation or alkylation. Thus, the addition of acetyl chloride to a benzene solution of  does not result in an increased yield of the ketone. Likewise, the addition of *n*-butyl chloride does not result in the formation of butylbenzene or butylacetophenone. When, however, an excess of aluminum chloride is also provided, only normal and *sec*-butylbenzenes are formed and not the alkylated acetophenone.[1]

It is important to note that when an attempt is made to carry out the concurrent alkylation and acetylation of benzene in the presence of slightly less than the calculated quantity of $AlCl_3$ required for acylation, in some instances, *e.g.*, *n*-butyl chloride, only acylation occurs despite the fact that this reaction requires molar proportions of the condensing agent, whereas only catalytic amounts are necessary for alkylations. This phenomenon is to be attributed to the preferential attachment of the aluminum chloride to the carbonyl group of the acylating agent as shown previously. The course of such competitive reactions depends, however, on the reactivity of the alkyl halide. When the highly reactive *tert*-butyl chloride is used instead of the normal halide under similar conditions, then alkylation as well as acylation occurs. Thus, acetyl chloride and *tert*-butyl chloride in benzene solution react exothermally, 30 to 80°C., to give *tert*-butyl- and *p*-di-*tert*-butylbenzenes in addition to acetophenone.[1] It is significant also, that when alkyl and acyl groups are both present in the same molecule, *e.g.*, ω-chloracetyl chloride ($ClCH_2COCl$), the acyl halide reacts preferentially with benzene to form the lachrymatory agent ω-chloroacetophenone. An excess of $AlCl_3$ does not activate the alkyl chlorine, again indicating the difficulty in causing the $\mathrm{ClR{\cdot}\underset{\underset{O\cdots AlCl_3}{\|}}{C}{\cdot}R'}$ addition complex to react further. This inactivity is precisely the opposite of the action of β-chloroethyl alcohol which leads to the formation of dibenzyl:

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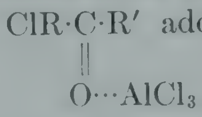
[1] GROGGINS and SWERN, Unpublished investigations, 1937.



$$ClCH_2CH_2OH + 2C_6H_6 \rightarrow C_6H_5CH_2CH_2C_6H_5$$

Effect of Other Halides.—Thomas showed that ferric chloride could be used not only as a condensing but also as a chlorinating agent for the preparation of halogenobenzenes.[2] He was able to prepare the entire series of chlorobenzenes (C_6H_5Cl to C_6Cl_6), by successive treatments with ferric chloride. The reaction was characterized by the liberation of hydrogen chloride and the reduction of the iron halide.

Boswell and McLaughlin found that the amount of hydrogen chloride evolved in the reaction of benzene with chloroform was a maximum when an equimolecular mixture of aluminum chloride and ferric chloride was used.[3] The liberation of the hydrogen chloride cannot, however, be used as an index of the catalytic activity of mixed halides in the preparation of alkyl aryl ketones, for it has been shown that the ferric halide may act as a chlorinating agent, this action being accompanied by the splitting off of the acid. In the isomerization of paraffins and cycloparaffins, however, where the presence of hydrogen chloride is essential, the use of mixed halides which contribute a greater quantity of HCl is advantageous. Ferric chloride as a minor constituent of aluminum chloride in the preparation of ω-chloroacetophenone exercises a catalytic activity that is not so great as that of aluminum chloride.[4]

A number of investigations have been made in which the operating efficiency of technical aluminum chloride, containing about 1.5 per cent of $FeCl_3$, was compared with that of a colorless, screened product. The reactions were carried out in an iron mill, using approximately the combining proportions of the reactants. Under such conditions, the results indicate that both products give substantially the same yields in the preparation of 4′-bromo-2-benzoylbenzoic acid.[5] In the preparation of alkyl aryl ketones, however, wherein the oily ketonic layer has to be separated from the hydrolyzed reaction mass, it has been found that the use of a purer aluminum chloride not only gives better yields but also affords a quicker and cleaner separation.

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[1] GROGGINS and SWERN, Unpublished investigations, 1937.

[2] THOMAS, *Compt. rend.*, **125,** 1211 (1898).

[3] BOSWELL, and MCLAUGHLIN, *Can. J. Research*, **1,** 400 (1929).

[4] MILLER, Edgewood Arsenal, U. S. War Department Report.

[5] GROGGINS, STIRTON, and NEWTON, *Ind. Eng. Chem.*, **23,** 893 (1931).

Riddell and Noller have made a comprehensive study of mixed catalysts in the Friedel-Crafts reaction.[1] They found that in the preparation of alkyl phenyl ketones from acid chlorides and benzene, the yields diminished as $AlCl_3$ is replaced by $FeCl_3$. When acid anhydrides were used for the similar preparation of the phenones, the yield decreases rapidly to a minimum, then rises to a maximum, and finally falls off to the value obtained with pure $FeCl_3$.

Effect of Size of Aluminum Chloride Particles.—In carrying out the Friedel-Crafts reaction, practical considerations would recommend the use of aluminum chloride in the form of granules or small lumps. As compared with powdered material, these would be less hygroscopic in storage and handling and less troublesome in delivering to the reactor,[2] and, finally, the larger particles would not react so readily, thus contributing to a better regulated initial reaction.

TABLE V.—PREPARATION OF 4′-CHLORO-2-BENZOYLBENZOIC ACID IN AN ENAMEL-LINED VESSEL. EFFECT OF SIZE OF $AlCl_3$ PARTICLES[1]

Atmospheric Pressure

Expt. No.	Kind $AlCl_3$	Yield, %	M. p., °C.
1	Lump, 15 to 20 mm. dia.	88.5	148.6
2	Pea size, 4 mm. dia.	92.5	148.4
3	Sand size, 0.5 to 1.0 mm. dia.	94.0	147.8
4	Powder	94.3	148.0

Reduced pressure to remove HCl

Expt. No.	Kind $AlCl_3$	Yield, %	M. p., °C.
1	Lump	88.9	147.6
2	Pea size	96.8	147.6
3	Sand size	96.0	147.0
4	Powder	97.0	148.0
5	Powder, containing 1.5% $FeCl_3$	96.2	148.0

[1] Phthalic anhydride (tech.), 296 gm. = 2 moles
Monochlorobenzene (b.p., 132°), 1,350 gm. = 12 moles
Aluminum chloride, 612 gm. = 4.6 moles, $AlCl_2$
Temperature, 50°C.; time, 5 hr.

In the preparation of alkyl aryl ketones and some keto acids, it is found that the effect of the size of aluminum chloride particles is closely related to the efficiency of the agitation.[3] With moderately good agitation, particles up to the size of a pea can be used with success in the preparation of keto acids. The data relating to the preparation of 4′-chloro-2-benzoylbenzoic acid are given in Table V.

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[1] RIDDELL and NOLLER, *J. Am. Chem. Soc.*, **54**, 290 (1931).

[2] GROGGINS, *Ind. Eng. Chem.*, **23**, 152 (1931).

[3] GROGGINS and NAGEL, *Ind. Eng. Chem.*, **25**, 1083 (1933).

Since the Friedel-Crafts synthesis can be employed for the preparation of hydrocarbons, aldehydes, ketones, etc., and may involve the use of gases or very volatile liquids as reactants, it is clear that different types of reaction require individual consideration. Possibly, the only general permissible conclusion is that practical and theoretical considerations favor the use of the coarsest material that gives satisfactory yields.

Removal or Addition of Hydrogen Chloride.—In most Friedel-Crafts syntheses, hydrogen halide is liberated as a volatile product of reaction. The quantity of the gas produced is closely proportional to the extent of the reaction,[1] and, with certain exceptions noted below, its removal is instrumental in accelerating the completion of the reactions. The preparation of acetophenone and ethylbenzene from the appropriate acyl and alkyl halides may be used to typify such syntheses:

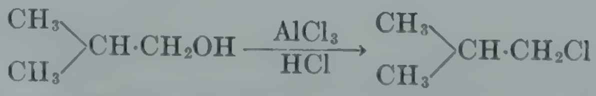
$$CH_3{\cdot}CO{\cdot}Cl + C_6H_6 \rightarrow C_6H_5{\cdot}CO{\cdot}CH_3 + HCl$$
$$C_2H_5Cl + C_6H_6 \rightarrow C_2H_5{\cdot}C_6H_5 + HCl$$

In the preparation of some ketones and keto acids, it is found that by maintaining a slightly reduced pressure in the reaction vessel, thereby drawing a slow stream of warm, dried air over the charge, practically theoretical yields are obtained. By referring to the previous Table V, it will be seen that the removal of the liberated hydrogen chloride exercises a beneficial effect in the preparation of 4′-chloro-2-benzoylbenzoic acid.

The preceding data and observations lead to the conclusions that in the liquid-phase Friedel-Crafts synthesis of keto acids and ketones, it is necessary to provide a practically homogeneous reaction mass and to remove the volatile product of the reaction, hydrogen chloride. The apparatus best suited for this purpose should, therefore, (1) provide thorough mixing; (2) scrape the walls of the reactor; and (3) break the surface of the reaction mass to facilitate the escape of the liberated hydrogen chloride.

In reactions catalyzed by alumimun chloride, wherein olefins, alcohols, and carbon monoxide are condensed, hydrogen chloride must be introduced in order to facilitate the formation of alkyl and formyl chlorides, respectively. The isomerization of paraffins and cycloparaffins likewise depends on the presence of hydrogen chloride. The following reactions should serve to indicate the need for a hydrogen halide as a coreactant.

1. Esterification of alcohols:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH{\cdot}CH_2OH \xrightarrow[HCl]{AlCl_3} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH{\cdot}CH_2Cl$$

---

[1] Numerous investigations have shown that the quantity of HCl liberated is in excess of amount combined in organic halides. This appears to be due to the degradation of AlCl$_3$, since the ratio of Cl to Al in the residue is low.

2. Isomerization of paraffins:

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \xrightarrow[HCl]{AlCl_3} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH{-}CH_3$$

3. Chlorination, by addition:

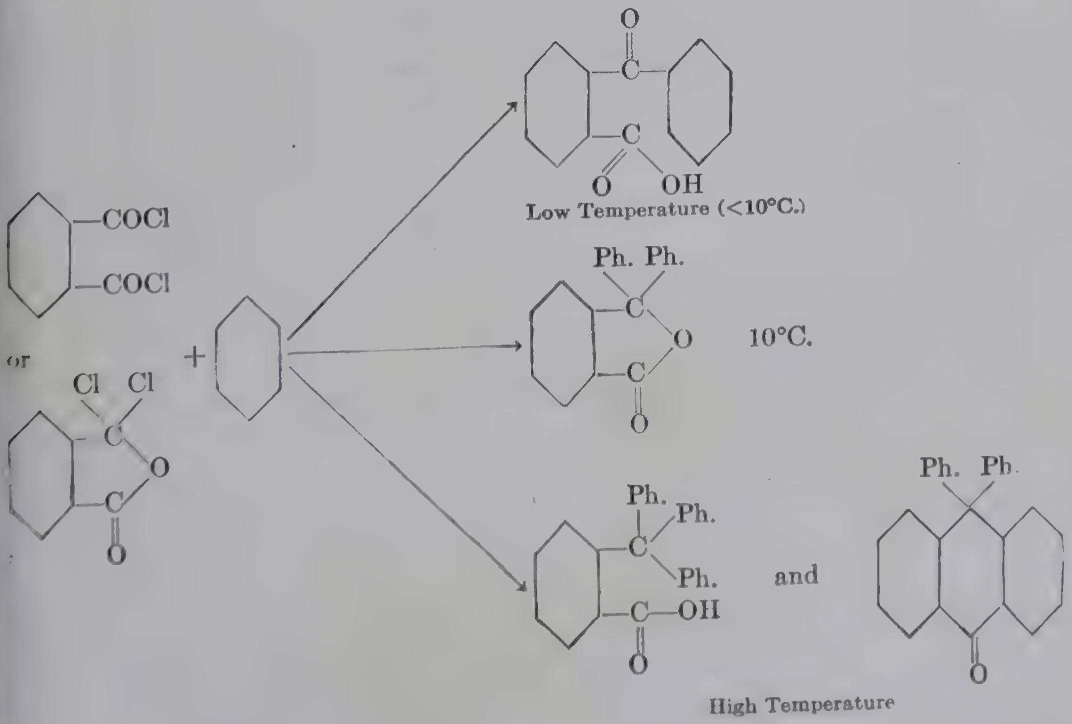
$$H_2C{:}CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

4. Combination:

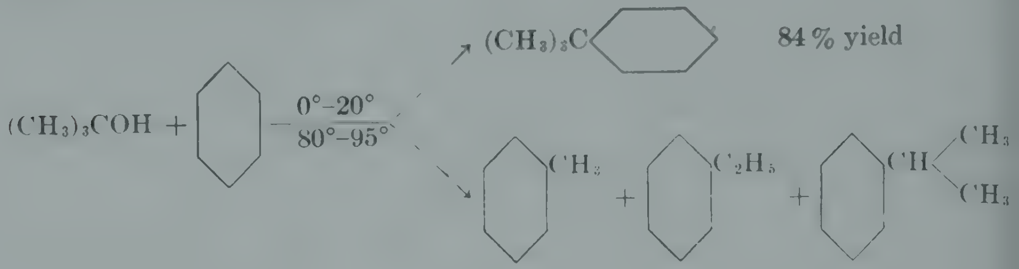
$$CO + C_6H_6 \xrightarrow[HCl]{AlCl_3} C_6H_5{\cdot}CHO$$

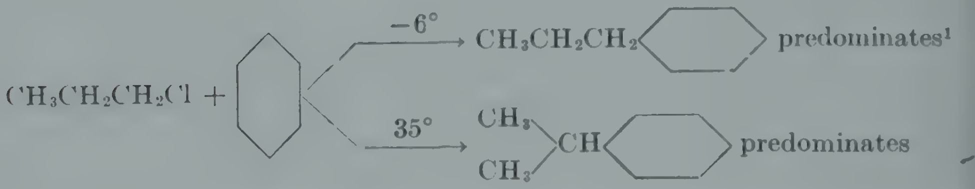
Effect of Temperature.—In organic synthesis, the general effect of operating at higher temperatures is to increase the rate of reaction. In some unit processes, *e.g.*, sulfonation of naphthalene, variations in temperature also affect the orientation of the new substituent. In Friedel-Crafts syntheses, these and other deep-seated changes occur when the reaction temperature is not rigidly controlled at the optimum for a particular synthesis. A moderate elevation in temperature may bring about secondary condensations which are accompanied by the splitting out of hydrogen chloride or water from 1 or 2 molecules. With excessive heating, almost all Friedel-Crafts reaction masses can be largely converted to oily or resinous masses of complex or uncertain constitution.

Phthalyl chloride reacts in its two isomeric forms with benzene in excess, to give benzoylbenzoic acid, diphenyl phthalide, *o*-triphenylmethylbenzoic acid, and 9-diphenylanthrone, depending on the temperature employed.



The condensation of *tert*-butyl alcohol and *n*-propyl chloride with benzene give similar results:





Most Friedel-Crafts reactions involving alkylation and acylation can be carried out below 100°C. When excessive temperatures are used in alkylations, there is a greater degree of disubstitution. In the Fries reaction, mild and drastic temperatures are conducive to the formation of para and ortho acylphenols, respectively. Similarly, in the preparation of thymol and carvacrol (see page 731), the equilibrium between desired products and unwanted isomers is appreciably affected by the temperature of reaction.

Effect of Solvents.—Friedel-Crafts syntheses are usually carried out in a fluid medium. Most frequently, as in the preparation of keto acids, alkyl aryl ketones, and arylalkanols, the solvent is an excess of the reacting aromatic hydrocarbon or substituted hydrocarbon. When a comparatively inert extraneous solvent is preferred or required, carbon disulfide finds favor, but tetrachloroethane and nitrobenzene are also used, particularly for reactions at higher temperatures. Liquid ethylene and propane are employed for low-temperature alkylations and polymerizations.

Although various solvents exert a significant influence on the course of some reactions, the principal functions are (1) to provide a practically homogeneous reaction mass and (2) to act as a good heat-transfer agent. There is difficulty in obtaining such a condition when highly reactive substances are condensed at low temperatures. Under such circumstances, substances of high solvent power for the organo-aluminum chloride complex are chosen, even when such solvents are known to be reactive in similar syntheses at higher temperatures. Thus, when benzene or *o*-dichlorobenzene is used as a vehicle for the preparation of α-naphthoylbenzoic acid, the liquid component serves merely as a solvent.

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[1] IPATIEFF, PINES, and SCHMERLING, *J. Org. Chem.*, **5**, 257 (1940).

for, in this instance, naphthalene reacts more readily and captures the phthalic anhydride-aluminum chloride complex. The data in Table VI show that a lower yield and inferior product are obtained when a less efficient or smaller quantity of solvent is employed.

In the chlorination of biphenyl and naphthalene with gaseous chlorine, it was shown that benzene could be used to advantage as a solvent. This similarity in operating technic is to be expected, since chlorination in the presence of a metal halide may reasonably be considered as a Friedel-Crafts reaction. The employment of normally reactive fluid substances as solvents for more highly reactive materials is not confined to aromatic compounds, for ethylene dichloride, carbon tetrachloride, and particularly tetrachloroethane have been used for this purpose.

Table VI.—Comparison of Solvents in Preparation of α-Naphthoylbenzoic Acid

No. Expt.	Reaction time, hr.	Reaction temp., °C.	Solvent	Solvent ratio	Solvent recovery, %	Yield N.B.A., %	M.p., °C.
1	2	15	C_6H_6	12:1	97	97.6	165 to 168
2	4	5	C_6H_6	6:1	97	95.0	150 to 160
3	5	0	C_6H_6	3:1	97	92.0	140 to 155
4	2	15	CS_2	12:1	90	95.0	145 to 155
5	4	5	CS_2	6:1	90	93.0	140 to 150
6	5	0	CS_2	3:1	90	92.0	135 to 145
7	2	15	$C_6H_4Cl_2(1, 2)$	12:1	99	97.5	167 to 170
8	4	5	$C_6H_4Cl_2(1, 2)$	6:1	99	97.0	168 to 171
9	5	0	$C_6H_4Cl_2(1, 2)$	3:1	99	97.5	170 to 172

Nitrobenzene finds use as a solvent because of (1) its excellent solvent properties; (2) its high boiling point; and (3) its ability to moderate, sometimes to a remarkable degree, the course of certain reactions. The moderating influence may be attributed to the fact that nitrobenzene forms a loose $AlCl_3$ complex and gives up the catalyst in a regulated fashion. Consequently, it is particularly useful in highly reactive condensations involving phenols, amines, and volatile acid chlorides. In the preparation of benzaldehyde from carbon monoxide and benzene, the use of nitrobenzene as a solvent makes possible carrying out the reaction at normal instead of 1,000 lb. pressure.

In the acylation of phenols, the relation between ortho and para derivatives can largely be controlled by the choice of a solvent. Thus, the use of nitrobenzene, which permits milder reaction conditions, results in the preponderant formation of para derivatives, whereas carbon disulfide is conducive to the formation of ortho hydroxy alkyl aryl ketones.

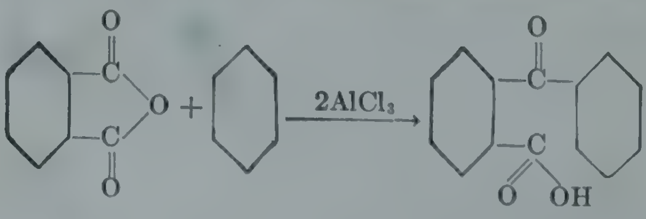
Hydrolysis of Reaction Mass.—In hydrolyzing the anhydrous aluminum chloride complex of ketones, keto acids, etc., it is best to keep the temperature of the suspension below the maximum used during the Friedel-Crafts condensation. This dictum applies whether the reaction has been carried out in the liquid phase in the presence of solvents or only combining proportions of the reactants are employed. When molecular proportions of the reactants are treated in a horizontal mill reactor, this step involves little difficulty. The powdered aluminum chloride complex is merely added slowly to the cold dilute acid in the hydrolyzer, which may be a wooden vessel, since there is no solvent to be recovered. In alkylations and isomerizations, the complex is obtained as a sludge which may be separated for reuse. Hydrolysis of the hydrocarbon fraction introduces no appreciable heat problem because of the low concentration of metal halide.

When a liquid reaction mass is hydrolyzed by the addition of mineral acid to the charge, there is danger that the temperature will mount to prohibitive levels before the charge is completely hydrolyzed. Such excessive heating is conducive to the formation of an impure product. In alkylations, most of the aluminum chloride is associated with unsaturated products at the base of the reactor and is generally reused. The supernatant saturated alkyl derivative, however, contains a small amount of catalyst after settling. In order to obviate undesirable reactions during subsequent distillation operations, the aluminum compounds may be precipitated by reaction with amines, etc., and removed.

CHEMICAL ENGINEERING PROBLEMS

A number of general chemical engineering problems are involved in the practical application of the Friedel-Crafts synthesis. To some extent, the nature of these problems can be forecast by a study of the theoretical and chemical aspects of the reaction. Efficient operation depends, largely, on (1) proper preparation and handling of reacting materials; (2) scientific design and construction of apparatus; and (3) control of the reaction so as to lead practically exclusively to the formation of the specific products desired.

Assuming, merely as a basis of discussion, that the synthesis relates to the preparation of *o*-benzoylbenzoic acids, which are the intermediate compounds in the manufacture of anthraquinone derivatives.



we may then expect to be confronted by the following considerations:

I. Handling of materials:
  - *A*. Anhydrous aluminum chloride.
  - *B*. Anhydrides and acid chlorides.
  - *C*. Aromatic hydrocarbon.
    1. Storage and transportation.
    2. Effects of moisture.
    3. Preparation for use in the reaction.

II. Design and construction of apparatus:
  - *A*. For reactions using molecular proportions of the reactants.
  - *B*. For reactions using an inert solvent or an excess of liquid aromatic hydrocarbon.
    1. Materials of construction.
    2. Mechanical devices for feeding the charge.
    3. Type of agitation.
       - (1) Relation of size of charge to size of vessel.
       - (2) Relation of size of charge to type of agitation.
    4. Discharging and hydrolyzing the reaction mass.

III. Control of Friedel-Crafts reaction:
  - *A*. Obtaining homogeneity.
  - *B*. Ensuring formation of intermediate addition compounds without deleterious by-products.
  - *C*. Maintaining anhydrous operating conditions.

Experience has shown that the preceding considerations are to a large extent common to all Friedel-Crafts syntheses, and detailed discussion of the idiosyncrasies of individual reactions does not appear necessary.

Handling of Materials.—When anhydrous aluminum chloride is packed in iron drums under conditions that ensure the absence of appreciable moisture, it may be stored for long periods or conveyed over long distances with safety. When, however, water is permitted to come in contact with it, hydrogen chloride is certain to be formed. The quantity of hydrogen chloride will depend on the amount of water and the degree of agitation of the halide. If sufficient moisture is present, particularly in the free space in the container or reaction vessel or at the point of contact with the outside atmosphere, then hydrochloric acid is formed. The presence of this acid leads to problems of corrosion.

The highly active acid anhydrides, acid chlorides, and alkyl halides are readily susceptible to hydrolysis. The absorption of moisture by these reagents results in compounds that are less active, require more aluminum chloride for condensation, and generally lead to lower yields of desired product. Furthermore, the ingress of moisture into storage containers for these active components usually results in corrosion problems.

In certain reactions, such as the isomerization of butane and the alkylation of isoparaffins, problems of handling anhydrous hydrogen chloride and gaseous hydrocarbons are encountered.

The aromatic hydrocarbons—benzene, toluene, naphthalene, etc.—offer no special corrosion problems and may, therefore, be stored in any suitable sealed containers.

Design of Apparatus. *Fluid Reactions.*—Most of the early investigators of the Friedel-Crafts synthesis carried out the reactions in a liquid medium. This procedure ensured a practically homogeneous reaction mass. When sufficient solvent or sufficient liquid vehicle was provided for the viscous intermediate reaction product, little difficulty was experienced in stirring the charge.

When aluminum chloride functions as a true catalyst, as in the synthesis of hydrocarbons, the reactants and final products are generally liquids, and no problem in merely rotating the agitator is encountered. In the preparation of ketones and keto acids, the formation of viscous intermediate addition compounds necessitates utilizing either an excess of the liquid aromatic reactant (benzene, toluene, chlorobenzene) or an extraneous inert solvent such as carbon disulfide, nitrobenzene, or tetrachloroethane. In some instances, where there is considerable variation in the reactivities of aromatic compounds at fixed temperatures, one can be used as a vehicle while the other enters into the reaction. Thus, Groggins and Newton successfully employed *o*-dichlorobenzene as the inert solvent in the Friedel-Crafts preparation of α-naphthoylbenzoic acid by condensing naphthalene with phthalic anhydride.[1]

In the preparation of keto acids, the reaction proceeds from the liquid stage to the viscous addition compound. During this transition, it is difficult to stir the charge with the usual vertical-type agitators unless a solvent or an inert diluent is employed to provide the necessary fluidity.

These considerations have led to the adoption of several types of apparatus for carrying out such syntheses. The older procedure involves the use of lead- or enamel-lined, jacketed, agitated vessels. In these (Fig. 1), the charge is kept fluid by the most desirable expedient, as previously indicated. The preparation of ω-chloroacetophenone or other alkyl aryl ketones usually follows this procedure. In Fig. 1 is shown diagrammatically the arrangement of the apparatus that is used.

It is obvious that the introduction of inert solvents or an excess of aromatic hydrocarbon entails an economic loss of considerable magnitude. It involves (1) cost of solvent recovery; (2) loss of solvent or equivalent; (3) increase in operating time; (4) more complex and more costly operating system; and (5) additional problems regarding corrosion.

When the solvent ratio is low, difficulty is experienced in drawing off the charge for hydrolysis. Consequently, this step must be carried out in the principal reaction vessel. Experience has shown that sooner or later flaws will develop in enamel linings, thus necessitating replacement.

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[1] Groggins and Newton, *Ind. Eng. Chem.*, **22**, 157 (1930).

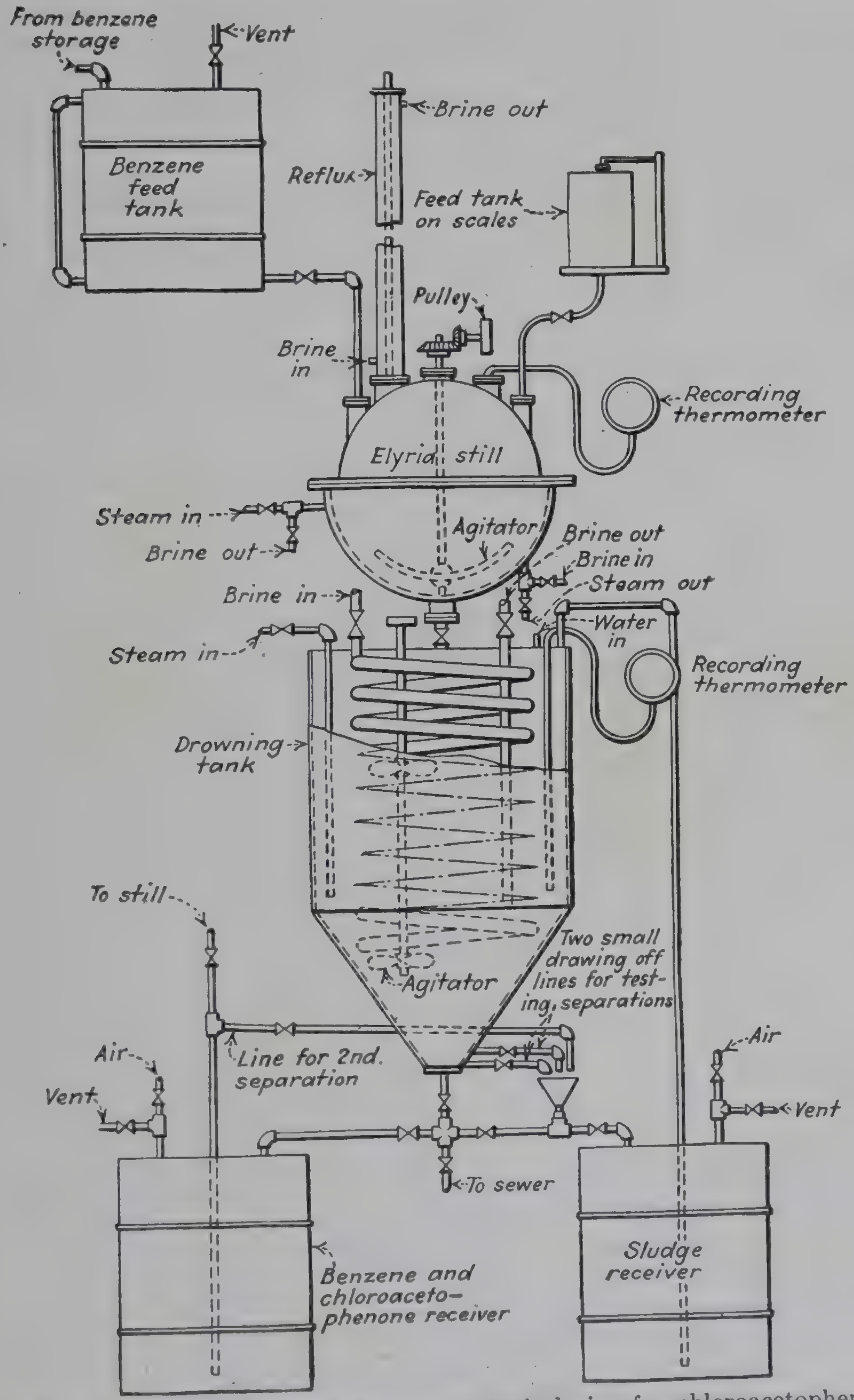
From benzene storage
Vent
Benzene feed tank
Brine out
Reflux
Feed tank on scales
Pulley
Brine in
Recording thermometer
Elyria still
Steam in
Brine out
Agitator
Brine out
Brine in
Steam out
Brine in
Water in
Steam in
Recording thermometer
Drowning tank
To still
Two small drawing off lines for testing, separations
Agitator
Air
Line for 2nd. separation
Air
Vent
Vent
To sewer
Benzene and chloroacetophenone receiver
Sludge receiver

FIG. 1.—Plant assembly for condensation and hydrolysis of ω-chloroacetophenone and other alkyl aryl ketones.

Molecular Reactions in Iron Reactor.—Appreciating the inherent deficiencies of the prior methods of operation, Stone and Jacobson utilized the apparatus shown in Fig. 2 for the preparation of keto acids.[1] This is essentially a horizontal rotary ball mill which is provided with inlet and outlet connections for solids, liquids, and gases, so that it constitutes a closed reactor. The reacting materials may be introduced in any desired sequence and then mixed at a temperature so low that practically no reaction takes place.

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[1] Stone and Jacobson, U. S. 1,656,575 (1928).

When a reaction vessel of this type is used, it is possible to employ approximately the molecular combining proportions of the reactant materials. This economical procedure now becomes feasible because practical homogeneity of the reaction mass is obtained by the grinding action of the balls or bars in the reactor. The rotary effect and grinding action of the iron weights thoroughly mix the reactants and, with proper control of temperature, a smooth and substantially complete reaction is obtained. The charge in the mill becomes viscous and porous during the intermediate stages of the reaction, even when all the reactants are solid.[1]

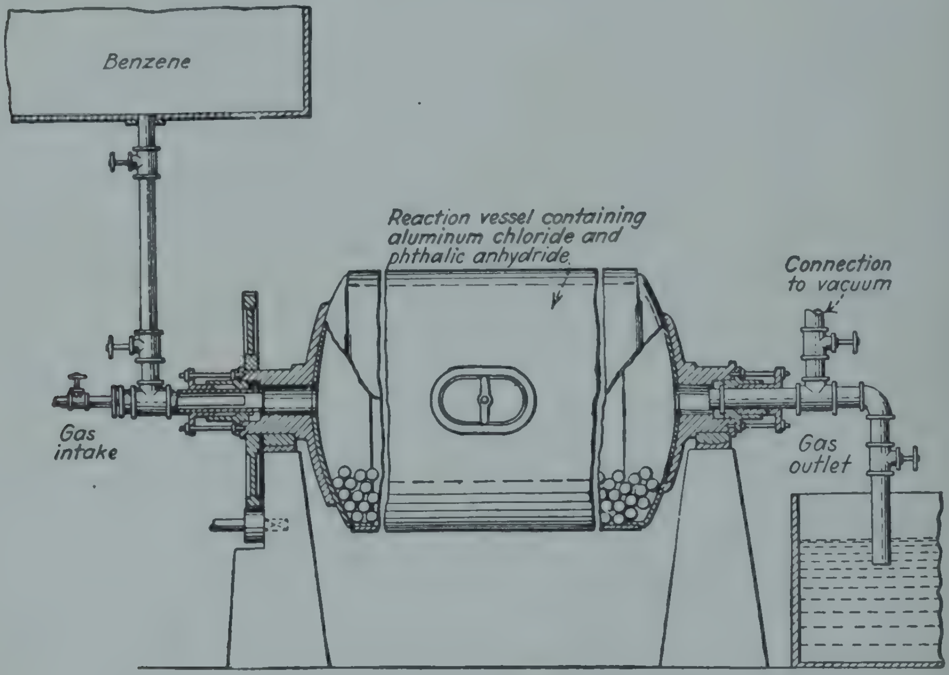
Benzene
Reaction vessel containing aluminum chloride and phthalic anhydride
Connection to vacuum
Gas intake
Gas outlet

FIG. 2.—Mill-type reactor for Friedel-Crafts reactions.

During this period, the din of the crushing mechanism becomes deadened. If insufficient balls are present, they will be enmeshed in the viscous charge, and no grinding action takes place. As the reaction progresses, the anhydrous aluminum chloride compound of the keto acid is formed and separates out as a fine colored powder.

That the aluminum chloride complex of the keto acid may be obtained as a freely flowing dry powder is a matter of great importance. This fact makes possible a division of operations, such as condensation in the reactor followed immediately or subsequently by hydrolysis in any suitable covered, agitated vessel. Since hydrolysis generally takes place in solutions that are slighlty acid with mineral acid, it is advisable to use vessels of wood, silicon iron, lead, or other suitable acid-resistant material for this operation. The dry, powdery, hygroscopic aluminum salt may be delivered to a dry, enclosed hopper, where it is cooled. It is then delivered in a regulated stream into the hydrolyzer, which contains cold, dilute mineral acid. The hydrolysis can therefore be easily controlled, so that the maximum temperature does not rise above the optimum for condensation. This precaution leads to the formation of purer products.

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[1] GROGGINS, *Ind. Eng. Chem.*, **22**, 620 (1930).

Probably the most important advantage in the use of the horizontal mill reactor is the practicability of using iron in its construction. When the necessary precautions have been observed, practically no free or combined moisture enters the reactor. Hydrogen chloride only is then liberated during the condensation. This will not attack iron to any appreciable extent, and laboratory experience has shown that this type of reactor will give satisfactory service over a long period of years. Replacements are necessary only at the connection where the hydrogen chloride is exhausted.

The size of the horizontal reactor must be considerably out of proportion to the weight of the reacting materials. This precaution is necessary in spite of the fact that molecular proportions of the reactants are taken. During the transition from the liquid to the viscous stage, the reaction mass becomes porous, owing to the liberation of hydrogen chloride. This spongy mass tends to fill the entire vessel. This phenomenon occurs even when the weight of the charge is only one-tenth the water capacity of the reactor. When pressure develops in the vessel, some of the spongy reaction mass oozes out into the hydrogen chloride exhaust line, which is at the horizontal axis of the reactor (Fig. 2).

Effect of Agitation.—The rate of reaction is, of course, a function of the efficiency of the stirring mechanism. In fact, mixing efficiency has a vital influence on the yield and purity of the product. Insufficient or inefficient mixing may lead to uncondensed reactants or to excessive reaction on heated surfaces.

In the condensation of biphenyl with phthalic anhydride according to the Friedel-Crafts reaction, it was found that the yields increased with the grinding efficiency (Table VII). The experiments are divided into three groups, as follows: (1) in a vertical, enamel-lined vessel fitted with an anchor-type agitator; (2) in a horizontal mill with insufficient agitation, *i.e.*, where the weight of iron blocks in pounds was one-third the water

TABLE VII.—EFFECT OF TYPE OF AGITATION IN PREPARATION OF 4′-PHENYL-2-BENZOYLBENZOIC ACID

Phthalic anhydride, 1 mole = 148 gm.; biphenyl, 1 mole = 154 gm.; aluminum chloride sublimed (10 per cent excess), 293 gm.; yield, theory, 302 gm.

Type of agitation	Temp., °C.	Time, hr.	Yield, gm.	Yield, %	Purity, %
Experiment I					
Agitated kettle	55 to 60	18	244	80.8	97.4
Mill with insufficient agitation[1]	55 to 60	20	278	91.1	97.6
Mill with efficient agitation[2]	55 to 60	18	290	96.0	97.8
Experiment II					
Agitated kettle	60 to 65	12	208	68.9	97.5
Mill with insufficient agitation[1]	60 to 65	12	239	79.1	97.8
Mill with efficient agitation[2]	60 to 65	12	292	96.7	98.0

[1] Ratio weight of iron blocks in pounds to water capacity of mill, 1:3.

[2] Ratio weight of iron blocks in pounds to water capacity of mill, 1:1.

capacity of the mill; and (3) when the weight of the iron grinding blocks was equal to the water capacity of the reactor.

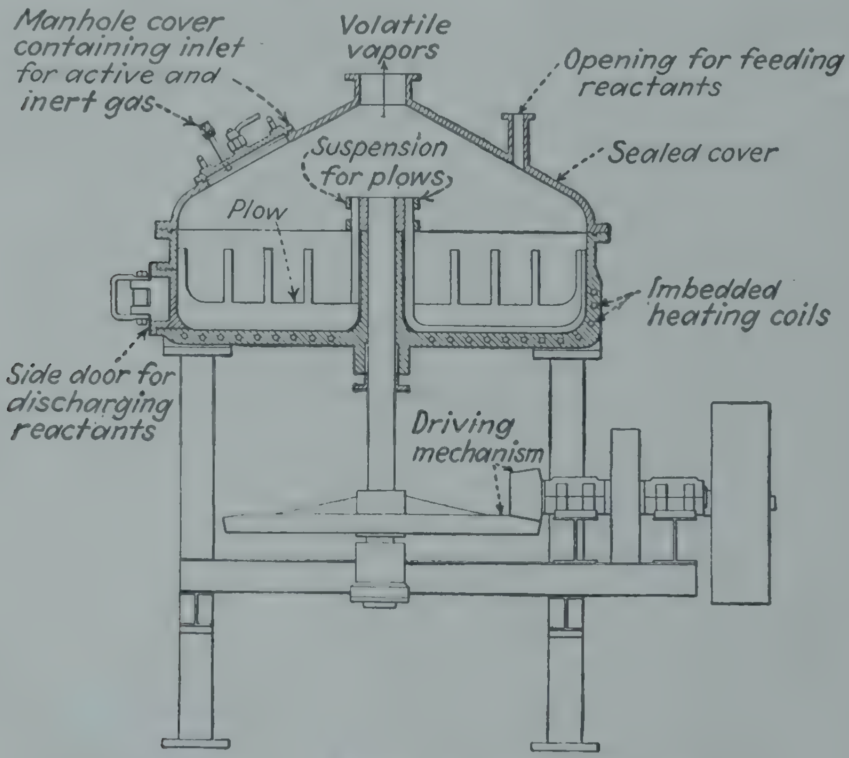
Manhole cover containing inlet for active and inert gas
Volatile vapors
Opening for feeding reactants
Suspension for plows
Sealed cover
Plow
Imbedded heating coils
Side door for discharging reactants
Driving mechanism

FIG. 3.—Reactor for carrying out Friedel-Crafts reactions.

A reactor[1] designed according to Fig. 3 is suitable for a wide variety of Friedel-Crafts syntheses. The vulnerable inside reaction compartment is preferably made of or lined with the newer alloys which are resistant to the corrosive action of hydrochloric acid and acid chlorides. Some of the advantages of such a reactor may be set forth as follows:

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[1] Groggins, U. S. 2,008,418 (1935).

1. *Homogeneity.*—The reactants may be introduced in a regulated manner while the stirrer is in motion. The modified plow (*a*) ensures positive agitation; (*b*) breaks the surface of the mass and thus facilitates the escape of the liberated hydrogen chloride; and (*c*) scrapes the walls of the vessel, thus providing satisfactory heat transfer.

2. *Removal or Retention of Hydrogen Chloride.*—By means of slightly reduced pressures or the passage of a current of dry air over the charge, the liberated gas can be removed conveniently from the upper portion of the reactor. When alkyl or acyl halides are formed as intermediate products of reaction through the intervention of hydrogen chloride, then the gas may be retained under the desired pressure.

3. *Operating Efficiency.*—Because the reactor permits initiating and concluding a reaction at any desired temperature and with any desired ratio of active or inactive fluid components, it makes possible efficient and economical operations.

4. *Physical Properties of Reaction Mass.*—By controlling the removal of the active or inactive fluid components under reduced pressure and by the aid of jacket heating, the reaction mass can be obtained as a nondusting granulated product or as a viscous to resinous paste. By means of the side door of the reactor which is sealed during the reaction period, the charge can be delivered to suitable containers for storage or to another vessel for subsequent treatment.

MECHANISM OF THE FRIEDEL-CRAFTS REACTION

Basic Concepts Regarding Mechanism.—In view of the fact that reactions catalyzed by metal halides may involve simple addition, double decomposition, hydrogenation and dehydrogenation, chlorination and dehydrochlorination, polymerization, isomerization, dehydration, inter- and intramolecular rearrangements, fission, etc., it is not difficult to understand why numerous theories have been suggested to explain the diverse reactions. Fortunately, theoretical explanations of the Friedel-Crafts reaction have kept pace with increased knowledge in the domains of physics and physical chemistry.

What appears to be common to the more tenable explanations are the following points:

1. The formation of binary ionized addition compounds (similar to solute-solvent complexes) which are characterized by conductivity. This is attributed to the fact that aluminum chloride is first and foremost an electron acceptor and causes atoms or groups coming within its orbit of influence to migrate with their bonding electrons so that there is a virtual conversion of a covalent to an electrovalent bond.

$$R\cdot CH_2{:}Cl + AlCl_3 \xrightarrow[\text{Shift}]{\text{Cl:}} R\cdot C\overset{+}{H}_2 \cdots Al\overset{-}{Cl}_4$$

$$R\cdot CO{:}Cl + AlCl_3 \xrightarrow[\text{Shift}]{\text{Cl:}} R\cdot \overset{+}{C}O \cdots Al\overset{-}{Cl}_4$$

2. The reaction of the highly ionized binary addition compound with a hydrocarbon, phenol, olefin, hydrogen, etc., to yield ternary complexes. This is attributed to the unstable character of $R\cdot \overset{+}{CH_2} \cdots AlCl_3\overset{-}{X}$ which attacks points of molecules in the chemical environment that facilitate electron exchange, thus:[1]

$$R\cdot C\overset{+}{H}_2 \cdots AlCl_3\overset{-}{X} + C_6H_5{:}H \rightarrow R\cdot C\overset{+}{H}_2 \cdots AlCl_3\overset{-}{X} \cdots \overset{+}{H}{:}C_6\overset{-}{H}_5$$

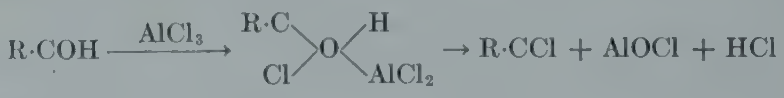
The preceding is merely a graphic picturization; and aside from the fact that we know that such ternary complexes are ionized and are good conductors, we have no definite information regarding the distribution of the charge. It is to be emphasized that the reactions of the binary complex $R\cdot \overset{+}{CH_2} \cdots AlCl_3\overset{-}{X}$ with its chemical environment may be (1) competitive, (2) concurrent, (3) concomitant, and (4) consecutive.[2]

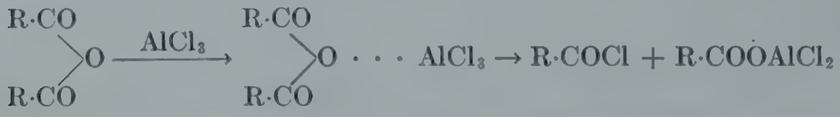
3. The rearrangement of the ionized ternary complex to one involving principal valences.

4. The dissociation of the complex into relatively stable compounds—usually with elimination of HX.

$$R\cdot C\overset{+}{H}_2 \cdots AlCl_3\overset{-}{X} \cdots \overset{+}{H}{:}C_6\overset{-}{H}_5 \rightarrow R\cdot CH_2\cdot C_6H_5 + AlCl_3 + HX$$

When the chemical environment contains no third component, stabilization of the binary complex may occur:





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[1] According to the electronic theory of acids and bases, $AlCl_3$ is an acid, *i.e.*, an electron acceptor, while benzene, which donates a share in a pair of electrons is a base. The formation of the coordinate bond is neutralization. See LUDER and ZUFFANTI, *Chem. Rev.*, **34,** 345 (1945); *J. Chem. Ed.*, **21,** 485 (1944); LUDER, *J. Chem. Ed.*, **22,** 301 (1945).

[2] According to Watson ("Modern Theories of Organic Chemistry"), "The simple collision theory has proved highly successful when applied to gaseous reactions, but attempts to extend the same conceptions to reactions in the liquid phase or in solution are at once met with the difficulty arising from lack of knowledge of the conditions existing in the liquid state. No complete interpretation of the effect of the solvent upon reaction velocity has as yet been reached; it is difficult, moreover, to estimate the extent to which the kinetic theory may be employed in solution, and further complications may arise owing to solvation phenomena, energy transfers due to collisions of solute with solvent molecules, ionization phenomena, and other causes."

Formation of Conducting Addition Complexes.—Meerwein has shown that many weak electrolytes are increased in strength by the formation of complex ions.[1] Although simple solvation leads to ionization of molecules as a precursor of electrolytic dissociation, in complex formation there is also the formation of a chemical bond between one of the potential ions and part of its environment. This union results in the nascence of an ion of larger radius and the same charge which is, consequently, less firmly bound to its fellow.

In Friedel-Crafts reactions involving acyl and alkyl halides, the addition complexes that are formed may be regarded as coordination compounds containing the complex anion $(\overset{-}{\text{AlCl}_4})$. Thus:

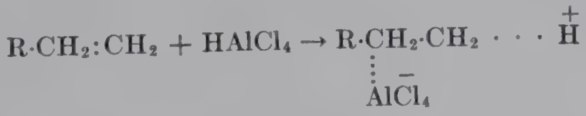
$$CH_3COCl + AlCl_3 \rightarrow (CH_3\overset{+}{CO}) \cdots (\overset{-}{AlCl_4})$$

According to Fairbrother, such a process constitutes effectively the conversion of a covalent carbon-chlorine bond into an ionic bond.[2] This transition appears to occur as the first step in acylation and alkylation reactions with appropriate halides. In the complex anion $(\overset{-}{\text{AlCl}_4})$, all the chlorine atoms concerned in the reaction should have an equal chance of escaping as hydrogen chloride. Fairbrother proved this experimentally be employing aluminum chloride in which part of the chlorine atoms were unstable isotopes, *i.e.*, radioactive. It was shown that an addition compound is formed in which the chlorine atoms leave the carbon atoms completely and enter the complex anion $(\overset{-}{\text{AlCl}_4})$ prior to the evolution of hydrogen chloride.

The formation of the electron donor $\overset{-}{\text{AlCl}_3\text{X}}$ as a precursor of reaction can reasonably be postulated for most Friedel-Crafts reactions, thus

Alkylation:

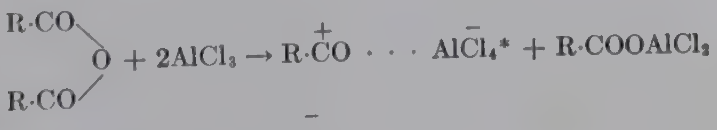
$$R{\cdot}CH_2Cl + AlCl_3 \rightarrow R{\cdot}\overset{+}{CH_2} \cdots \overset{-}{AlCl_4}$$



$$R{\cdot}CH_2{:}CH_2 + HAlCl_4 \rightarrow \underset{\overset{\vdots}{\overset{-}{AlCl_4}}}{R{\cdot}CH_2}{\cdot}CH_2 \cdots \overset{+}{H}$$

Acylation:

$$R{\cdot}COCl + AlCl_3 \rightarrow R{\cdot}\overset{+}{CO} \cdots \overset{-}{AlCl_4}$$



$$\begin{matrix} R{\cdot}CO \diagdown \\ \quad O \\ R{\cdot}CO \diagup \end{matrix} + 2AlCl_3 \rightarrow R{\cdot}\overset{+}{CO} \cdots \overset{-}{AlCl_4}{}^{*} + R{\cdot}COOAlCl_3$$

---

[1] Meerwein, *Ann.*, **455**, 227 (1927).

[2] Fairbrother, *J. Chem. Soc.*, **1937**, 503.

* The indicated attachment of $AlCl_4$ to oxygen is intentional and is our method

Isomerization:

$$R\cdot CH_2\cdot CH_3 + HAlCl_4 \rightarrow R\cdot CH_2\cdot \overset{+}{C}H_2 \cdots Al\overset{-}{C}l_4$$

Carboxylic Acids and Aldehydes:

$$O{=}C{=}O + 2AlCl_3 \rightarrow AlCl_2O\overset{+}{C}O \cdots Al\overset{-}{C}l_4$$

$$C{=}O + HAlCl_4 \rightarrow \overset{+}{H}CO \cdots Al\overset{-}{C}l_4$$

Alcohols.—Although tertiary alcohols react via alkyl chlorides,

$$(CH_3)_3COH \xrightarrow{AlCl_3} (CH_3)_3CCl$$

alkylations with primary alcohols may presumably proceed by at least two mechanisms.

$$R\cdot CH_2OH + HAlCl_4 \rightarrow R\cdot \overset{+}{C}H_2 \cdots Al\overset{-}{C}l_4 + H_2O \qquad (1)$$

$$R\cdot CH_2OH + AlCl_3 \rightarrow R\cdot CH_2O \cdots AlCl_2 + HCl \qquad (2)$$

The first mechanism gives an alkyl halide type of addition compound and should lead to a branched-chain derivative. When the $AlCl_3$ ratio is relatively low and the HCl is permitted to escape preponderantly unchanged, alkyl substitution would probably occur.

Conductivity of Solute-solvent Complexes.—Wohl and Wertyporoch, by means of electrical conductivity measurements, have succeeded in clarifying a number of mooted questions regarding the formation of metal halide complexes.[1,2] The appearance of conductivity is first to be traced to the formation of solute-solvent complexes.[3] When aluminum bromide is added to ethyl bromide, it is found that the conductivity increases from the negligible value $K < 3 \times 10^{-9}$ to 1.206×10^{-4} for a 20 per cent solution. The measurements for dilute solutions involve a time factor until equilibrium is reached. For concentrated solutions, the final conductivity per mole of $AlBr_3$ is quickly reached and is practically constant ($\mu = 0.1$, compared to $\mu = 10$ for the more soluble $(C_2H_5)_4NBr$ in ethyl bromide). The specific conductivities of the acetyl and benzoyl chloride addition complexes in ethyl bromide are as follows:

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of explaining why $AlCl_3$ is attached during the reaction to the carbonyl $> C = O$ group and why there is here no shift along the carbon skeleton which results in rearrangements as in the carbonium ion $R\cdot \overset{+}{C}H_2$.

[1] Wohl and Wertyporoch, *Ber.*, **64**, 1357 (1931).

[2] Wohl and Wertyporoch, *Ann.*, **481**, 34 (1930).

[3] Hein and Schramm [*Z. physik. Chem.*, **151**A, 234 (1930)] made similar observations with a solution of lithiumethyl in zincethyl.

Complexes	$K \cdot 10^7$		
	Normal conductivity	0.08 mole $AlCl_3$ per liter	0.2 mole $AlCl_3$ per liter
Benzoyl chloride	3.0	1,020	2,000
Acetyl chloride	3.2	5,500	16,170

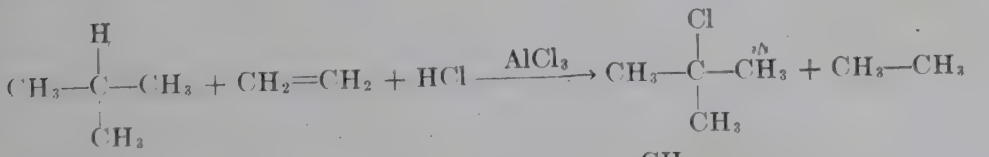
According to Wertyporoch and Firla, *Ann.* **500**, 287 (1933).

The fact that stable, stoichiometric addition products of alkyl halide and aluminum halide have not yet been isolated does not preclude their existence in the course of the reaction. It should be remembered that stable, easily isolated compounds do not possess catalytic character and that the instability that makes isolation difficult constitutes the precise attributes for catalytic effectiveness of the intermediate compound.

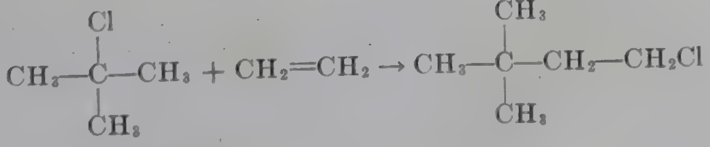
An intermediate, particularly when it exists in equilibrium in a very limited concentration, may fully determine the course of the reaction through its decomposition, for it is the most unstable component of the equilibrium. "What seems to be required is not a stable compound, but rather a body in or on which, by dissociation or otherwise, there is an active kinetic exchange of linkages between the catalyst proper and the component toward which affinity is exerted."

Mechanism of Alkylation of Paraffins.—Several mechanisms for the catalytic alkylation of paraffins have been postulated. A recent proposal suggests that the reaction proceeds via the conversion of the paraffin to an alkyl halide.[1] The mechanism is outlined below for the reaction of isobutane with ethylene. Similar reactions occur with other paraffins and olefins.

The *tert*-butyl chloride formed in Eq. (3) starts a new cycle by reacting with ethylene as in Eq. (2). Ethane is produced only in the initiating step, and the amount formed will therefore be small.



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 + CH_2{=}CH_2 + HCl \xrightarrow{AlCl_3} CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 + CH_3-CH_3 \qquad (1)$$



$$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 + CH_2{=}CH_2 \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2Cl \qquad (2)$$

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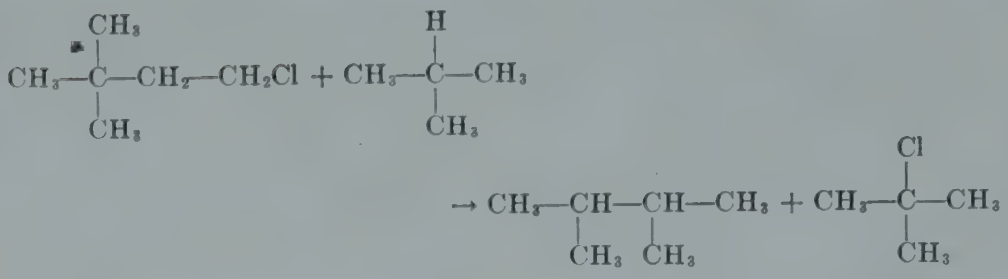
[1] Schmerling, *J. Am. Chem. Soc.*, **66**, 1422 (1944).



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2Cl + CH_3-\underset{CH_3}{\overset{H}{C}}-CH_3 \rightarrow CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3 + CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_3 \quad (3)$$

Striking confirmation of the first step [Eq. (1)] is found in the work of Bartlett, Condon, and Schneider.[1] These investigators found that the conversion of isopentane to *tert*-amyl bromide and the transformation of *tert*-butyl chloride to isobutane take place readily. Butyl and other halides enter into similar reactions with other paraffins, and halogen from the metal halide is found in the newly formed alkyl halide.

According to Bartlett, the *tert*-butyl positive ion is capable of stripping off a hydrogen—in this case, a tertiary one—with its pair of bonding electrons, thus saturating the butyl fragment as isobutane and leaving a *tert*-amyl positive ion in its place. On isolation of the product, this appears as a halide, the halogen coming from reunion with the AlX_4 ion which accounts for the formation of the *tert*-amyl bromide.

$$(CH_3)_3CCl + AlCl_3 \rightleftharpoons (CH_3)_3\overset{+}{C} + Al\overset{-}{Cl_4}$$

$$(CH_3)_3\overset{+}{C} + C_2H_5(CH_3)_2CH \rightleftharpoons (CH_3)_3CH + C_2H_5C(CH_3)_2^{+}$$

$$C_2H_5C(CH_3)_2^{+} + Al\overset{-}{Cl_4} \rightleftharpoons C_2H_5(CH_3)_2CCl + AlCl_3$$

This process is analogous to an intramolecular rearrangement in which the hydrogen migrates with its bonding pair of electrons from one carbon to an adjacent one carrying an open sextet. The only difference is that, in the reaction now visualized, the shift of the "hydride" particle occurs at a collision between two different molecules.

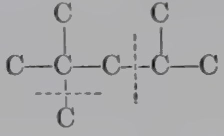
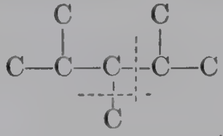
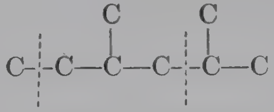
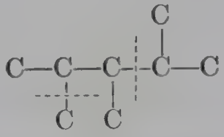
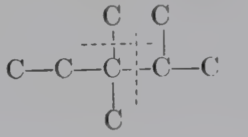
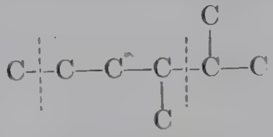
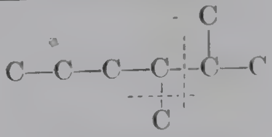
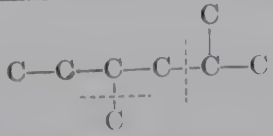
Based on their studies on the alkylation of isobutane with the lower olefins, Gorin and coworkers have suggested the following mechanism of alkylation.[2]

There are two major steps in the mechanism. (1) The catalyst and the olefin form an addition complex *via* coordination with two electrons from the double bond, and (2) the addition product reacts with isobutane to produce the final product and release the catalyst. In step 2 the isobutane molecule is assumed to behave as if it becomes polarized into a negative methyl fragment and a positive isopropyl fragment as it approaches the olefin-catalyst complex; the reaction is completed by the

[1] BARTLETT, CONDON, and SCHNEIDER, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

[2] GORIN, KUHN, and MILES, *Ind. Eng. Chem.*, **38**, 795 (1946).

MECHANISM OF ALKYLATION OF ISOBUTANE WITH ISOBUTENE, 2-BUTENE, AND 1-BUTENE

Olefin	Initial form of olefin-catalyst complex	Permissible forms of olefin-catalyst complex	Product obtained by addition of CH_3— and $CH_3—\overset{+}{C}H—CH_3$ to given form of olefin-catalyst complex
$\begin{array}{c}CH_3\\ H_3C:\ddot{C}::CH_2\end{array}$ Isobutene	$H_3C:\overset{CH_3}{\ddot{C}}\ :\ \underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\boxed{+-}$	$H_3C:\overset{CH_3}{\ddot{C}}\ :\ \underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\boxed{+-}$	 2,2,4-Trimethylpentane
		$H_3C:\underset{H}{\overset{CH_3}{\underset{\cdot\cdot}{\ddot{C}}}}\ :\ \overset{H}{\underset{\cdot\cdot}{\ddot{C}}}:\boxed{+-}$	 2,3,4-Trimethylpentane
		$H:\overset{H}{\ddot{C}}:\underset{H}{\overset{CH_3}{\underset{\cdot\cdot}{\ddot{C}}}}\ :\ \underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\boxed{+-}$	 2,4-Dimethylhexane
$H_3C:\overset{H}{\dot{C}}::\overset{H}{\dot{C}}:CH_3$ 2-Butene	$H_3C:\overset{H}{\ddot{C}}:\underset{CH_3}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\ \boxed{+-}$	$H_3C:\overset{H}{\ddot{C}}:\underset{CH_3}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\ \boxed{+-}$	 2,3,4-Trimethylpentane
		$H_3C:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\underset{CH_3}{\underset{\cdot\cdot}{C}}:\ \boxed{+-}$	 2,3,3-Trimethylpentane
		$H:\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\underset{CH_3}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\ \boxed{+-}$	 2,3-Dimethylhexane
$H_3C:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\overset{H}{\ddot{C}}::CH_2$ 1-Butene	$H_3C:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\overset{H}{\ddot{C}}:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\boxed{+-}$	$H_3C:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\overset{H}{\ddot{C}}:\boxed{+-}$	 2,3-Dimethylhexane
		$H_3C:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}}:\boxed{+-}$	 2,4-Dimethylhexane

addition of the negative methyl group to the carbon atom deficient in electrons, with the positive isopropyl group displacing the catalyst. The formation of the olefin-catalyst complex is illustrated for the case of isobutene, 2-butene, and 1-butene in the accompanying chart. The catalyst, which may be liquid hydrogen fluoride, sulfuric acid, or an aluminum halide, is represented by the symbol $\boxed{+-}$, in order to indicate its own polar structure.

The exponents of this mechanism contend that it permits accurate prediction of the products of alkylation and is successful in explaining the formation of all primary products so far established in isobutane alkylation.

Mechanism of Isomerization.—According to a number of investigators, the isomerization of alkanes in the presence of metal halides and hydrogen halides involves charged particles of extremely short life.[1] Using HBr and $AlBr_3$ to represent the applicable hydrogen halides and metal halides the following reactions are believed to occur:[2]

1. Carbonium ions are formed in two ways, by reaction of hydrogen bromide with an olefin or by reaction of bromine with hydrocarbon:

$$(CH_3)_2CH{=}CH_2 + HBr \rightarrow (CH_3)_2CHBrCH_3$$
$$(CH_3)_3CH + Br_2 \rightarrow (CH_3)_3CBr + HBr$$

The aluminum bromide catalyzes both these reactions. Alkyl bromides react with aluminum bromide to form the final ions:

$$(CH_3)_3CBr + AlBr_3 \rightleftarrows CH_3)_3C^+ + AlBr_4^-$$

2. The carbonium ion substitutes a hydride ion with fresh *n*-butane:

$$CH_3CH_2CH_2CH_3 + (CH_3)_3C^+ \rightleftarrows CH_3CH_2C^+HCH_3 + (CH_3)_3CH$$

3. The *n*-butyl carbonium ion is not stable and reverts to the *tert*-butyl carbonium ion:

$$CH_3CH_2C^+HCH_3 \rightarrow (CH_3)_3C^+$$

Thus the reaction becomes a chain reaction. The branched C_4 hydrocarbon in step 1 can be replaced by the normal type without difficulty. The important factor in the reaction is to have a source of carbonium ions. This was demonstrated by Pines and Wackher[1] who showed that, when an aluminum halide-hydrogen halide catalyst is used, the presence of olefins is necessary for isomerization to occur at moderate temperatures.

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[1] Whitmore, *J. Am. Chem. Soc.*, **54**, 3274 (1932); *Ind. Eng. Chem.*, **26**, 94 (1934)
Ingold, *Chem. Ind.*, **57**, 112 (1937).
Ipatieff, Pines, and Schmerling, *J. Org. Chem.*, **5**, 253 (1940).
Bartlett, Condon, and Schneider, *J. Am. Chem. Soc.*, **66**, 153 (1944).
Schmerling, *J. Am. Chem. Soc.*, **66**, 1422 (1944).
Bloch, Pines, and Schmerling, *J. Am. Chem. Soc.*, **68**, 153 (1946).
Pines and Wackher, *J. Am. Chem. Soc.*, **68**, 595 (1946).
Oblad and Gorin, *Ind. Eng. Chem.*, **38**, 822 (1946).

[2] Oblad and Gorin, *loc. cit.*

Oblad and Gorin have found that oxygen and bromine are effective promoters for aluminum bromide in the isomerization of *n*-butane and attribute their efficacy to their role in forming butyl halides, which, as shown above, act as a source of carbonium ions.[2] The advantageous use of oxygen may stem from the formation of HOBr, which adds on to olefins to form alkyl halides or haloolefins, thus promoting the reaction.

TECHNICAL SYNTHESES

Treatment of Hydrocarbons

Alkylation of Isobutane with Isobutene.—Alkylation of isoparaffinic hydrocarbons with olefins may be effected by Friedel-Crafts catalysts such as aluminum chloride and boron trifluoride.[3,4] The presence of a hydrogen halide is advantageous because it aids in isomerizing normal paraffins to branched chains and accelerates the conversion of olefins to alkyl halides. As indicated previously, a number of competitive reactions occur, and the resultant alkylate depends largely on the specific operating conditions.

Isobutane and an olefin (*e.g.*, butenes) can be condensed in the presence of aluminum chloride deposited on granular ceramic ware which is contained in a reactor. Part of the reacting isobutane is directed through a chamber containing the metal halide and thus provides a solution of the catalyst in the less reactive component.

As shown in Fig. 4, the process is carried out as follows:[5] A hydrocarbon fraction containing isobutane is delivered to the operating system by pump 1. Part of the feed is directed to the heater where the temperature is raised to approximately 125°C. and thence to a catalyst pickup chamber. By means of liquid flow and introduction of recycled hydrogen chloride, the quantity of metal halide made available as catalyst can be closely controlled. The effluent from the catalyst chamber is combined with the balance of the isoparaffinic charge which travels through line 2 and the olefins and recycled hydrogen and hydrogen chloride which are introduced under pressure through separate inlets. Mixing of the reactants is largely accomplished in line 3 leading to the packed reactor, which is maintained at 200 lb. per sq. in. and at 40 to 70°C. Provision

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[1] Pines and Wackher, *loc. cit.*

[2] Oblad and Gorin, *loc. cit.*

[3] See chapter on Alkylation for discussions relating to mineral acids as alkylating catalysts.

[4] See previous sections for discussions of isomerization and mechanism of reaction.

[5] Danforth, U. S. 2,342,123 (1944).

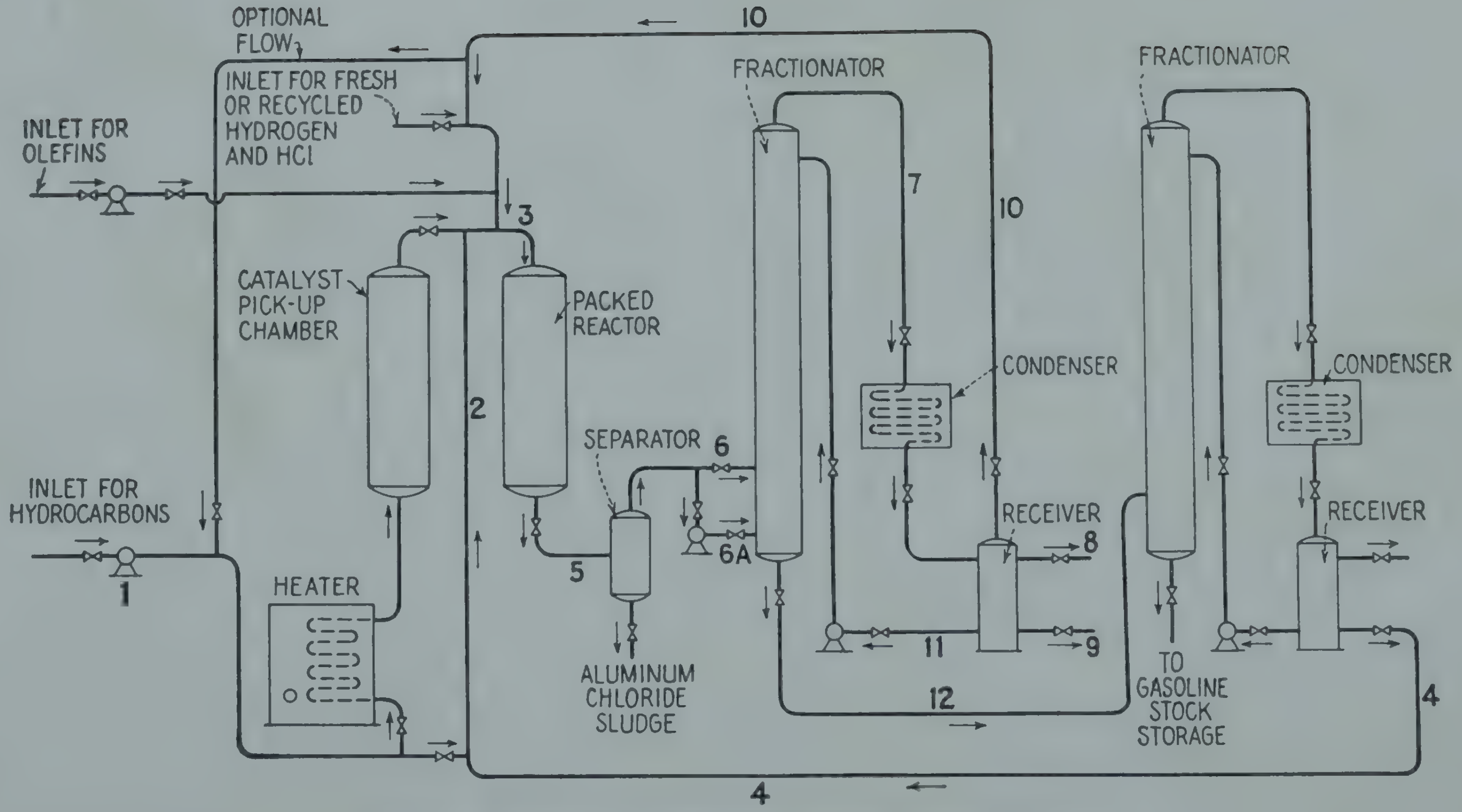
OPTIONAL FLOW
10
INLET FOR FRESH OR RECYCLED HYDROGEN AND HCl
INLET FOR OLEFINS
FRACTIONATOR
FRACTIONATOR
7
10
3
CATALYST PICK-UP CHAMBER
PACKED REACTOR
CONDENSER
CONDENSER
2
SEPARATOR
6
INLET FOR HYDROCARBONS
RECEIVER
RECEIVER
6A
8
1
5
HEATER
11
9
ALUMINUM CHLORIDE SLUDGE
12
TO GASOLINE STOCK STORAGE
4
4

FIG. 4.—Alkylation of isoparaffinic hydrocarbons with olefins.

is made for the recycling of unconverted isoparaffins, which are returned from the second fractionating column via line 4 and united with fresh material in line 2. Hydrogen chloride may be added to the isobutane entering the catalyst chamber to induce solution of the catalyst as well as isomerization of any hydrocarbons.

The products from the reactor are directed through line 5 and are cooled en route to a separator in which the organo-aluminum chloride complex is settled and then separated. The heavy aluminum chloride sludge can be used to treat fresh reactants and will thus give up olefinic hydrocarbons which are bound up with the spent aluminum chloride. Incidentally, some isomerization of the isoparaffins may also be effected.

The effluent from the separator which contains a substantially saturated alkylate formed from olefins and a portion of the isoparaffinic hydrocarbons as well as the excess of isoparaffins, hydrogen, and hydrogen chloride is led to a fractionator either through line 6 or 6*A* when the fractionation is made under pressure.

A light fraction containing hydrogen, hydrogen chloride, small quantities of methane, ethane, etc., is taken overhead through line 7 and delivered to a condenser and thence to a receiver which is equipped with gas release, line 8, and a liquid drawoff, line 9. Part of the gaseous mixture is recycled through line 10 and either reenters the system at the designated gas inlet or may be added to the portion of the isoparaffins directed through the catalyst pickup chamber. A portion of the condensed liquid in the first receiver is returned through line 11 to a point near the top of the fractionator to assist in controlling the temperature therein.

From the bottom of the first column, a substantially saturated alkylate plus unconverted isoparaffins is obtained. These are sent via line 12 to a second fractionating column from which unconverted isoparaffins are removed overhead. The distillate is condensed and led to a receiver. Here, part of the distillate is used for recycling over the fractionating column, and part returned through line 4 to the reactor. The higher boiling product which is withdrawn from the base of the fractionator contains the alkylate corresponding to gasoline motor fuel.

In the alkylation of isobutane with isobutene in the presence of freshly volatilized aluminum chloride which was continuously deposited upon a ceramic packing material, the results shown in Table VIII were obtained. The data indicate that the lower temperatures give greater yields of lower boiling materials having low bromine numbers. Thus, in period 6, operating at 38°C. (100°F.), the liquid product contained 73 per cent by volume of hydrocarbons boiling below 150°C., whereas the product from an 85°C. (185°F.) alkylation contained only 29 per cent by volume of a 150°C. end-point fraction. The octanes contained in the

38° alkylate were equivalent to 27.4 per cent of the total alkylate, had an octane number of 83.8, contained only 0.02 per cent chlorine, and had a bromine number of 5.

Isomerization of *n*-Butane.—Numerous methods of effecting the isomerization of paraffins have been proposed, but each type of process has its limitations and difficulties.[1] To appreciate better the problems of design and operation of an isomerization unit, it is desirable to review briefly the principal procedures that have been used.

TABLE VIII.—ALKYLATION OF ISOBUTANE WITH ISOBUTENE

	Period No.					
	1	2	3	4	5	6
Duration, hr	96	24	24	24	24	48
Temperature of packed reactor, °F	150	150	130	170	185	100
Pressure of packed reactor, lb./sq. in.	200	220	220	220	250	250
Charging stock, composition, mole %:						
Isobutane	70.9	70.6	71.0	70.9	69.7	70.0
n-Butane	16.5	16.4	16.6	16.5	16.7	16.7
Propane	2.0	2.0	1.9	2.0	2.5	2.4
Pentanes	0.0	0.0	0.0	0.0	0.5	0.5
Isobutene	8.4	9.0	8.5	8.5	9.0	8.9
Hydrogen chloride	2.2	2.0	2.0	2.1	1.6	1.5
Charging rates:						
Paraffin feed, cc./hr	198	203	201	195	203	206
Isobutene feed, cc./hr	19.5	21.3	20.0	19.2	21.4	21.6
Hydrogen chloride, g./hr	1.75	1.60	1.60	1.60	1.35	1.35
Mole ratio, isobutane/isobutene	8.4	7.9	8.4	8.4	7.8	7.8
Mole ratio, total butanes/isobutene	10.4	9.7	10.3	10.3	9.6	9.7
Liquid products, pentanes and higher hydrocarbons:						
Grams	1,517	384	313	275	309	1,024
Yield, based on isobutene charged weight %	157	144	126	115	116	190
Bromine number	21	10	28	36	42	7

The early methods employed a reaction chamber filled with lump or supported aluminum chloride as catalyst. When the catalyst was spent, it had to be replaced; and in order to obviate intermittent operations, a plurality of interconnected chambers was used. In such a fixed-bed type of operation, the catalyst was unevenly used, because the portion nearest the feed inlet became exhausted first. Furthermore, since the isomerization of paraffins is an exothermic reaction, it was difficult to control the temperatures within large-diameter beds, and hot spots invariably developed with a consequent rapid local degradation of the catalyst.

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[1] See partial list of patents on pp. 753, 754.

A better type of isomerization process involves an intimate contacting of reactants in the liquid phase with a liquid organo-aluminum chloride catalyst. Such a catalyst is usually made by treating a mixture of hydrocarbons with the metal halide, and the resultant sludge is a dark mobile liquid having a specific gravity of about 1.5. Hydrogen chloride is added as a coreactant to accelerate the isomerization reaction, and hydrogen and the lower alkanes are introduced as inhibitors to prevent excessive cracking.

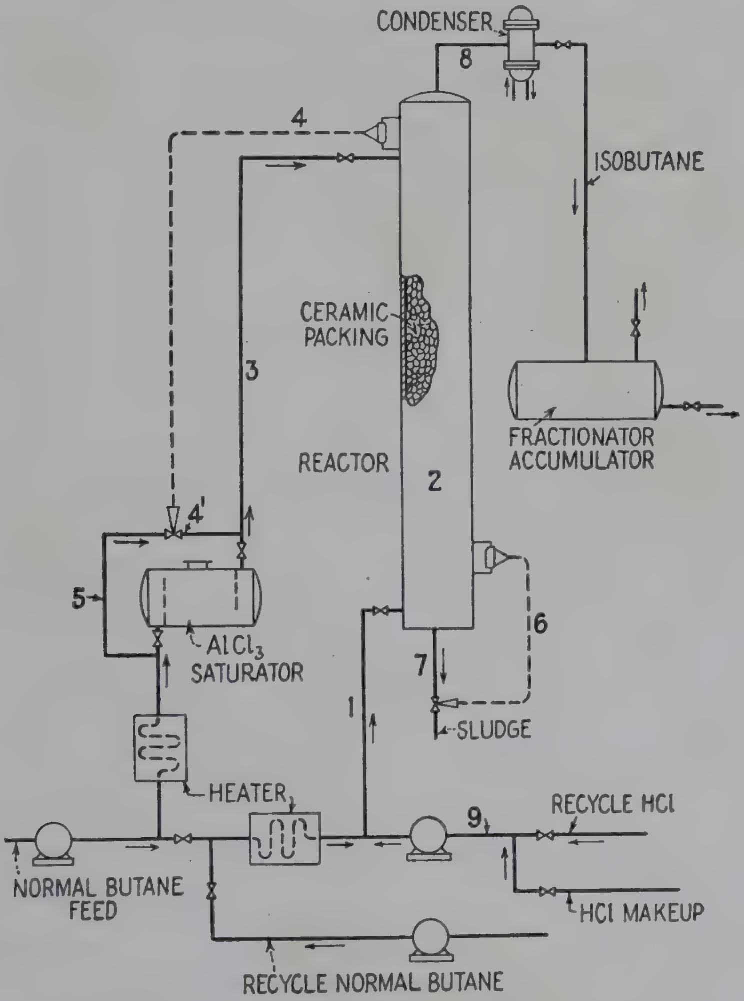
CONDENSER
8
4
ISOBUTANE
CERAMIC PACKING
3
FRACTIONATOR ACCUMULATOR
REACTOR
2
4'
5
6
$AlCl_3$ SATURATOR
7
1
SLUDGE
HEATER
9
RECYCLE HCl
NORMAL BUTANE FEED
HCl MAKEUP
RECYCLE NORMAL BUTANE

Fig. 5.—Butane isomerization unit.

Evering and coworkers have described industrial operations involving the use of liquid catalyst, the plants being designed to use diverse feed stocks and to produce isobutane, isopentane, or neohexane as the principal product.[1]

Recycling of the hydrocarbons contributes greatly to the formation of branched-chains and concomitant improvement in the octane number of the derived alkylate. The catalyst sludge from such operations is deposited largely in accumulator drums from which it is returned to the reactor along with fresh aluminum chloride. However, an appreciable loss of catalyst goes along with the treated hydrocarbons and is eventually removed by washing with alkaline solutions.

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[1] Evering, Fragen, and Weems, *Chem. Eng. News*, **22**, 1898 (1944).

The isomerization of paraffins can also be carried out continuously under conditions wherein the reaction mixture contains both liquid and vapor phases.[1] According to Henry, the normal butane to be converted is dried and pumped to the isomerization unit (Fig. 5), and is mixed with butane that is being recycled. The combined feed passes through a heater, where it is brought to a temperature of about 105°C. The heated hydrocarbons, now partly or entirely vaporized, are contacted with fresh or recovered hydrogen chloride. The reactants are delivered through line 1 into reactor 2 through a distributor and pass upward through the column of boiling hydrocarbons containing the catalyst.

A portion of the *n*-butane is directed through a heater to an aluminum chloride saturator. This stream carries a controlled quantity of dissolved metal halide through line 3 to the top of the reactor and thus provides a continuous supply of make-up catalyst.

A level of boiling butanes is maintained near the top of the reactor by control devices 4 and 4′, which also permit the entry of butane via line 5 which by-passes the $AlCl_3$ saturator. These streams are appropriately connected so as to dilute the butane-$AlCl_3$ effluent from the saturator and thus prevent premature deposition of the catalyst. Of the aluminum chloride entering the reactor, a portion is precipitated on the Raschig rings owing to the vaporization of isobutane. The balance remains suspended in the boiling butanes. The catalyst gradually forms a liquid organo-$AlCl_3$ sludge, which, because of its greater density, flows down over the packing countercurrent to the ascending stream of liquid and vaporous butane. The spent sludge becomes less viscous toward the lower part of the reactor owing to depletion of $AlCl_3$ and the higher prevailing temperatures. A reservoir of liquid sludge catalyst is maintained at the base of the reactor which acts on butanes entering through line 1 and aids in removing any catalytic poisons such as water, sulfides, and carbon monoxide. The completely spent sludge catalyst is drawn off continuously or intermittently through lines 6 and 7.

The isomerization presumably takes place in the catalyst-containing liquid phase; but owing to the fact that isobutane has a lower boiling point than *n*-butane (-10.0 *vs.* $-0.6°$), the desired iso compound is vaporized preferentially and removed from the reaction zone. During the flow of the butanes upward through the reactor, the concentration of isobutane increases, the temperature decreases, and the activity of the catalyst increases, thus providing conditions of time, temperature, and catalyst concentration favorable for efficient isomerization.

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[1] Henry, U. S. 2,366,028 (1944); Leonard, U. S. 2,366,117 (1944).

Pressure is maintained on the reactor so as to keep liquid butanes in the system at temperatures from 95 to 110°C. The vaporized effluents pass via line 8 to a condenser and thence to an accumulator tank from which the condensate is delivered to a fractionating column. The overhead from the fractionator which contains all the hydrogen chloride and some hydrogen, methane, and ethane is recycled to the reactor via line 9.

The performance of a plant as described above during a period of 5 weeks continuous operation gave the results shown in Table IX below.

TABLE IX.—TECHNICAL ISOMERIZATION OF *n*-BUTANE

HCl concentration in bottoms feed	6 mole %
$AlCl_3$ (free and combined) concentration in reactor	15–19 lb./cu. ft. reactor vol.
Top reactor temperature	205–210°F. (96–99°C.)
Bottom reactor temperature	220–225°F. (104–107°C.)
Top reactor pressure	240–245 lb./sq. in. gauge
Bottom feed rate	85–96 bbl./day/sq. ft. reactor cross section
Average conversion to isobutane	39 liquid vol. %
Average conversion to propane	1 liquid vol. %
Average conversion to pentanes plus	1 liquid vol. %
Catalyst life	0.71 lb./bbl./isobutane produced

Preparation of Ethylbenzene.—In technical operations, ethylene is substituted for ethyl chloride in the alkylation of benzene. The olefin is introduced into a suspension of aluminum chloride in benzene that has been saturated with hydrogen chloride and maintained at about 60°C. To ensure maximum contact, it is desirable to have a relatively tall reactor in which the ethylene is caused to pass upward through a large body of reaction liquor.

Although the principal product is ethylbenzene, considerable diethylbenzene is formed (Fig. 6), the quantity depending on the proportions of the reactants and other factors such as temperature and mixing. Inasmuch as such alkylations are reversible, the polyethylbenzenes are returned to ensuing batches. It is also convenient to use the higher boiling alkylbenzenes in combination with the aluminum chloride complex as a bath through which carburetted vapors of benzene and ethylene are bubbled.[1] The liquid in the reactor is kept at 140 to 150°C., which is above the boiling point of ethylbenzene but below the boiling point of the higher alkyl derivatives. The distillate thus obtained contains benzene, ethylbenzene, and some diethylbenzene. The fractionated ethylbenzene is delivered to a still for further purification, while the other components are returned to the reactor.

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[1] U. S. 2,364,203 (1944); FRANCIS and REID, *Ind. Eng. Chem.*, **38**, 1194 (1946).

When ethylbenzene is made on a large scale or in a continuous manner as an intermediate for the production of styrene, it is cumbersome to resort to the washing procedure for the removal of entrained catalyst. On the other hand, if the alkylbenzene is distilled in the presence of dispersed or dissolved catalyst, the organo-metal halide tends to catalyze decomposition and rearrangements. The yield of ethylbenzene will thus be reduced, and the volatilization of the aluminum chloride complex leaves deposits of scale and tars on the heated surfaces of the distilling apparatus.

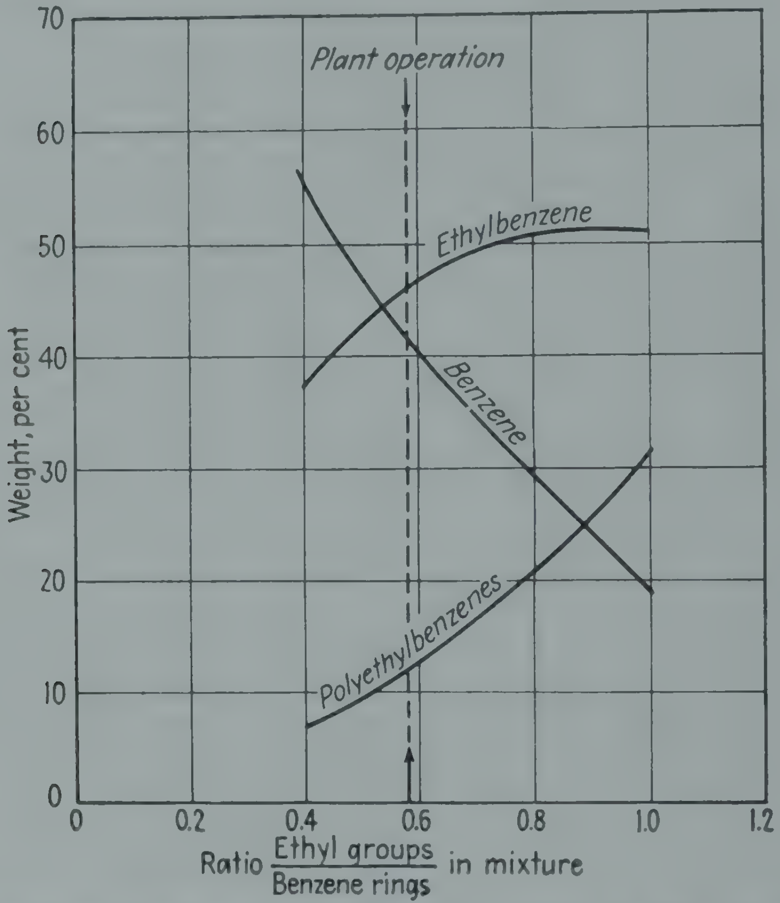

FIG. 6.—Equilibrium relations in the ethylation of benzene at 95°C. using aluminum chloride as catalyst. (*According to Mitchell, loc. cit.*)

To obviate washing and drying of the alkylbenzene and to avoid the undesirable effects of traces of the catalyst, the alkylation liquor is first separated from the bulk of the organo-aluminum chloride complex. The crude alkylbenzene is treated with an agent that is known to form relatively stable insoluble complexes with $AlCl_3$. Among such compounds are alkalene oxides, pyridine, ammonia, and amines.[1] The catalytic

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[1] U. S. 2,246,007 (1941).

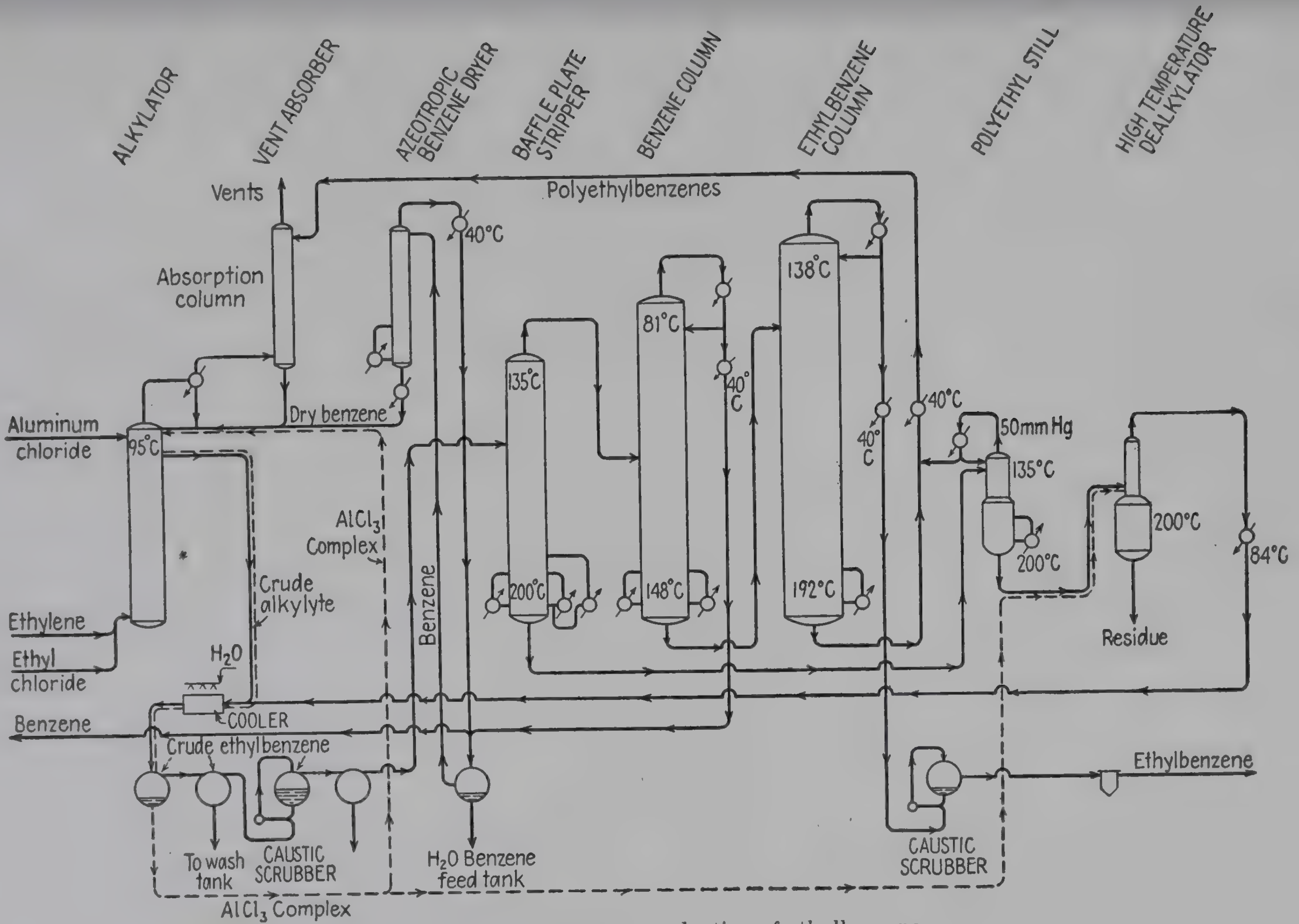
ALKYLATOR
VENT ABSORBER
AZEOTROPIC BENZENE DRYER
BAFFLE PLATE STRIPPER
BENZENE COLUMN
ETHYLBENZENE COLUMN
POLYETHYL STILL
HIGH TEMPERATURE DEALKYLATOR
Vents
Polyethylbenzenes
Absorption column
40°C
Aluminum chloride
95°C
Dry benzene
135°C
81°C
138°C
40° C
40° C
40°C
50mm Hg
135°C
200°C
200°C
84°C
AlCl₃ Complex
Crude alkylyte
Benzene
200°C
148°C
192°C
Ethylene
Ethyl chloride
H₂O
COOLER
Benzene
Residue
Crude ethylbenzene
Ethylbenzene
To wash tank
CAUSTIC SCRUBBER
H₂O Benzene feed tank
CAUSTIC SCRUBBER
AlCl₃ Complex

FIG. 7.—Flow diagram: production of ethylbenzene.

complex is thus rendered inactive and can be either settled or filtered off prior to the distillation of the alkylbenzenes.

The Dow process for making ethylbenzenes has been described by Mitchell.[1] Benzene dried by azeotropic distillation is fed in excess into an alkylating tower (Fig. 7) where it comes in contact with anhydrous aluminum chloride delivered by a screw conveyor. A metered quantity of ethylene as reactant is then used to pick up ethyl chloride and carry it to the reaction zone for use as a catalyst promoter.

The alkylators operate with a liquid depth of about 34 ft. Circulation is provided by the gas-lift effect of the ethylene entering at the base of the reactor. The aluminum chloride combines with the hydrocarbons to form a reddish brown, oily complex which is practically insoluble in the hydrocarbon layer. A representative composition would be

$AlCl_3$ (combined)	26%
$AlCl_3$ (free)	1%
High-molecular-weight hydrocarbons	25%
Benzene and ethylbenzene	48%

The reaction proceeds smoothly with negligible loss of ethylene. The exothermic alkylation is held at 95°C. by means of an overhead condenser and cooling water running down the outside of the shell. Aromatic hydrocarbons are removed from the effluent vapors by absorption. The crude alkylate, along with entrained complex, is cooled to about 40°C. and delivered to a large horizontal cylindrical tank where the aluminum chloride complex settles out and is then pumped (– – – lines) to the dealkylator or back to the alkylator. The crude ethylbenzene is decanted once more in a second horizontal tank and sent to a caustic scrubbing system where it is mixed with a 50 per cent caustic solution and allowed to settle. Another horizontal tank serves to remove any entrained caustic solution.

The crude, sweetened ethylbenzene is charged to a baffle-plate stripping column, heated with steam at 400 lb. pressure. The higher molecular-weight materials (Fig. 6) are withdrawn at the botton of the stripping still at 200°C. and delivered to the "polyethyl" still. The overhead from the stripper at 135°C. enters the benzene column, containing 20 plates, as a vapor feed. The excess benzene used in the reaction is distilled at 81°C. and ½ lb. pressure and returned to the wet benzene feed tank. Bottoms from the benzene column, consisting of ethylbenzene and high boilers, are fed to the ethylbenzene column. This column contains 58 plates and operates with a 3 to 1 reflux ratio and a top pressure of ½ lb. The distilled ethylbenzene is cooled to 40°C. and is obtained as a product of over 99 per cent purity. It is then scrubbed with a 20 per cent caustic solution and dried by passing through a bed of flake caustic. The yield of ethylbenzene based on benzene is 95.5 per cent.

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[1] MITCHELL, *Trans. Am. Inst. Chem. Eng.*, **42**, 293 (1946).

The bottoms from the baffle-plate stripper are delivered to the polyethyl still, containing 10 plates, which operates at 50 mm. Hg absolute pressure and a top temperature of 135°C. The overhead from this column is combined with the bottoms from the ethylbenzene column, cooled to 40°C., and then used as an absorption fluid in the alkylator vent recovery system. These polyethylbenzenes pass through a small absorption column, picking up aromatics and some of the ethylene and hydrogen chloride in the vents and returning them to the alkylator. The polyethyls are here dealkylated to ethylbenzene.

Bottoms from the polyethyl still are sent to a high-temperature dealkylator where they are subjected to reaction by the aluminum chloride complex at 200°C. The higher alkylate is broken down to benzene, ethylbenzene, and diethylbenzene, which pass overhead, leaving a tarry aluminum chloride residue.

Preparation of *tert*-Butylphenols. *Using* (1) *Butyl chloride;* (2) *Butyl alcohol.*—A mixture consisting of approximately equimolecular quantities of *tert*-butyl chloride and phenol, containing 1 per cent by weight of aluminum chloride, is caused to react in a jacketed, agitated vessel. The reaction is started at about 15°C., and the temperature of the charge is gradually raised to 100°C. After completion of the reaction, the product is cooled to 90°C., and a 50 per cent solution of sodium carbonate equivalent to 4 per cent of the weight of the reactants is added to the charge under agitation.

The contents of the reactor are filtered hot, and the filtrate is distilled through a fractionating column. The distillate consists of 10.5 per cent unreacted phenol, 12 per cent 2-*tert*-butylphenol, 70.2 per cent 4-*tert*-butylphenol, and 7.1 per cent 2, 4-di-*tert*-butylphenol.

The conversion of 2-*tert*-butylphenol to the isomeric para compound may be carried out as follows: A mixture consisting of 92.5 parts (1 mole) of *tert*-butyl chloride, 94 parts (1 mole) of phenol, 150 parts (1 mole) of 2-*tert*-butylphenol, and 6 parts of aluminum chloride is stirred in a suitable reactor at 25°C. for 1 hr. The temperature is then gradually brought up to 100°C. during the next hour. The reaction mass is then neutralized by the addition of 22 parts of sodium carbonate in 10 parts of water, and the charge filtered and distilled. The distillate consists of 224 parts (1.49 moles) of 4-*tert*-butylphenol, 13 parts (0.087 mole) of 2-*tert*-butylphenol, and 15 parts (0.073 mole) of 2, 4-di-*tert*-butylphenol. The 4-*tert*-butylphenol is obtained in 74.5 per cent of the theoretical yield based on the combined quantities of phenol and 2-*tert*-butylphenol used.

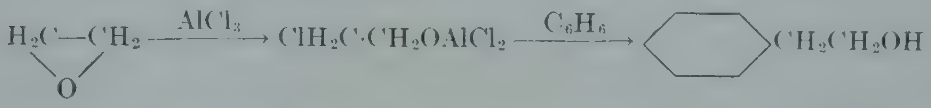
Because of the danger of losing some of the volatile butyl chloride (b.p., 51°C.) by entrainment with the liberated hydrogen chloride, it is desirable to have the reactor equipped with an efficient reflux condenser and to run under a slight pressure.

Instead of the butyl chloride, *tert*-butyl alcohol may be employed in the preparation of alkylphenols. Although the alkyl halides require only catalytic quantities of $AlCl_3$, the alcohols require approximately 50 molar per cent $AlCl_3$ in order to effect the conversion of the alcohol to the reactive alkyl chloride. The reactants are suspended in an inert solvent such as petroleum ether maintained at 30 to 50°C. The maintenance of a slight pressure on the reactor appears desirable.

The alkylphenols are useful antiseptics and germicides.[1] When *Staphylococcus* is used as the testing organism, the phenol coefficients of some of these compounds are as follows:

Material	Phenol Coefficient
Phenol, U.S.P.	1.0
tert-Butylphenol	87.5
Cresol, U.S.P.	3.1
tert-Butylcresol	75.0
Xylenol	5.6
tert-Butylxylenol	150.0

Preparation of β-Phenylethyl Aclohol.



The synthesis may be carried out in a glass-lined, agitated vessel provided with a jacket for circulated brine. An apparatus similar to a "Hough" or sleeve-and-propeller nitrator is, however, preferable, because success in this exothermic reaction depends largely on satisfactory temperature control. The reactor is charged with 150 parts (1 mole + 10 per cent) of pea-size aluminum chloride and 390 parts (5 moles) of benzene. Then 44 parts (1 mole) of gaseous ethylene oxide is gradually introduced in such a manner that minimal volumes of the diffused gas come into contact with a large volume of the liquid contents at a temperature of about 0°C. The introduction of air into the reactor facilitates the removal of hydrogen chloride and also serves to remove some of the heat of reaction and thus tends to inhibit the formation of chlorohydrin, β-phenylethyl chloride, and dibenzyl. The magnitude of such impurities depends on the control of factors that lead to side reactions. The charge is stirred for about 1 hr. after the ethylene oxide has been added and is then delivered to a vessel containing about 1,000 parts of iced water.

After separation, the water layer is run off, and the benzene solution of β-phenylethyl alcohol is washed with 150 parts of 2 per cent sodium carbonate. Upon ordinary distillation, the excess of benzene is removed and recovered, and the aromatic alcohol is then obtained by distillation *in vacuo*. The yields are in excess of 75 per cent of the theoretical.

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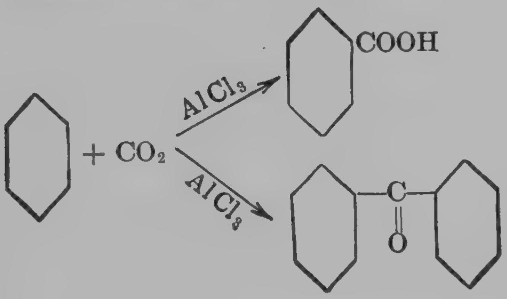
[1] Stockelbach, U. S. 2,081,284 (1937).

When used in the manufacture of perfumes, the crude β-phenylethyl alcohol must be freed from harsh-smelling impurities, and esterification of the alcohol in benzene solution has been found suitable for this purpose. The boric, phthalic, and oxalic esters are relatively nonvolatile, and their distillation and subsequent hydrolysis result in a relatively pure product.[1]

CARBOXYLIC ACID SYNTHESIS

Treatment of Benzenoid Compound with Carbon Dioxide.



When benezenoid derivatives are treated under pressure with carbon dioxide in the presence of aluminum chloride, the principal product of reaction is a derivative of benzoic acid.

In British Patent 307,223 are shown the methods of synthesizing benzoic acid and its derivatives. Of interest in these reactions is the fact that aromatic ketones of the benzophenone series are simultaneously formed. The condensation may be carried out in the following manner:

A high-pressure autoclave, fitted with stirrers, is charged with 100 parts of benzene and 50 parts of anhydrous alumnium chloride, the air being expelled by the repeated introduction of carbon dioxide under pressure and subsequent expansion; finally, carbon dioxide is brought therein under a pressure of about 60 atmos., and the contents heated to 100°C. while stirring. After from 12 to 15 hr., the surplus carbon dioxide is discharged, the viscous reaction product is decomposed with ice, and this product, after the addition of concentrated hydrochloric acid, is extracted with benzene. After the benzene is distilled off, a gray cake of crude benzoic acid remains which contains a considerable amount of benzophenone.

The initial benzene may be replaced by other aromatic hydrocarbons or their derivatives, such as chlorobenzene, toluene, xylenes, and chlorotoluenes.

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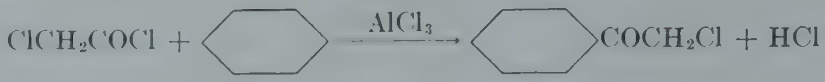
[1] Klipstein, U. S. 2,068,415 (1937).

Ketone Synthesis

Condensations with Aliphatic and Aromatic Acid Chlorides.—*ω-Chloroacetophenone.*



The preparation of ω-chloroacetophenone, which is described below, is similar to the procedure for making acetophenone or any of the alkyl aryl ketones. The condensation involves bringing benzene and an acyl chloride together in a suitable, agitated vessel provided with a reflux condenser.

In charging the reactor, which is an enamel-lined, jacketed vessel, 378 lb. of benzene is delivered from the feed tank (Fig. 1, page 773), and 160 lb. of anhydrous aluminum chloride is added, the agitator being kept in motion to prevent caking. The kettle is closed, and the circulation of brine through the jacket started.

When the temperature of the material in the kettle reaches 25°C., the addition of chloroacetyl chloride is started. The rate of feed is governed by the heat-transfer capacity of the jacket in maintaining the operating temperature at 25°C. Ordinarily, about 1½ hr. is required to introduce the required 142 lb. of chloroacetyl chloride. After the reactants are added, the temperature of the charge is raised to 60°C. by replacing the brine in the jacket with steam or hot water. This temperature is maintained for 2 hr. to permit the completion of the reaction. The charge is then drowned.

The drowning tank is prepared by introducing about 550 gal. of water, which is cooled to 5°C. by the brine coil (Fig. 1). The agitator on the drowning tank is started, and the charge from the reactor is delivered at such a rate that the temperature does not exceed 15°C. The reactor is then washed out with 50 lb. of benzene, the washings also being delivered to the drowning tank underneath. The agitation in the drowning tank is continued for 30 min. to ensure thorough mixing. A jet of live steam is then introduced into the mixture to bring the temperature up to 35°C. in order to facilitate subsequent separation. The charge is now permitted to stand until the constituents form into layers.

The separation of the upper benzene-chloroacetophenone layer from the lower water and sludge is of importance, because the presence of the metal halide during subsequent distillation operations would be deleterious. The aqueous solution of aluminum salt is run off and discarded. Any intermediate layer is withdrawn for further separation, while the benzene-chloroacetophenone layer is delivered to a blow case. Before distilling, the composite of several charges of ω chloroacetophenone is again treated with benzene, agitated, and settled in order effectively to remove any remaining contaminating aluminum compounds.

The distillation of the benzene-chloroacetophenone solution for the recovery of the ketone in a pure state may be accomplished either by vacuum distillation or by distillation with steam.

When distillation under reduced pressure is employed, the charge, consisting of approximately 70 per cent benzene and 30 per cent ketone, is first warmed to 80°C. to remove the benzene. The temperature is then raised by jacket heat to 105°C., to remove any water that may have been present. The still is now connected to the vacuum pump, so that a vacuum of 25 in. of Hg is attained. The water that was circulated through the condenser jacket is now drained, and steam is passed through it. The distillation of chloroacetophenone is indicated by the sudden rise in temperature on the still head, at which time the steam on the condenser jacket is shut off. The ketone distills over at 155 to 160°C. When the temperature drops to 125°C., the distillation is complete. A precaution should be taken finally to warm the condenser tube with steam, to ensure that any crystallized ω-chloroacetophenone is removed.

When the chloroacetophenone is recovered by distillation with steam, the benzene is first removed by jacket heat and delivered to its receiver. The temperature of the still is then raised to 165°C., and live steam introduced. The still temperature is gradually raised to 190°C., and the distillation continued until the condensate shows the absence of ketone. When this method of distillation is employed, very little tarry residue is left in the still. The ratio of steam to ketone distilled is approximately 2:1 by weight.

Condensations with Aliphatic Acid Anhydrides. *General Procedure.* A solution of 1 mole of aromatic hydrocarbon or derivative in carbon disulfide or preferably in an excess of aromatic reactant is placed in a suitable vessel provided with an agitator, reflux condenser, and vent for the liberated hydrogen chloride. To this solution is added 3.3 moles of powdered aluminum chloride ($AlCl_3$), and then, with rapid stirring, 1 mole of the aliphatic acid anhydride is slowly added. After all the acid anhydride has been introduced, the charge is heated by jacket heat until the evolution of hydrogen chloride is practically nil. The reaction mixture is then cooled to room temperature and decomposed by pouring into iced dilute mineral acid.

The ketone may be separated by permitting the aqueous suspension to separate into layers, discarding the aqueous solution of the metal halide, and working up the aromatic ketone by ordinary distillation to remove the aromatic reactant and then by distillation *in vacuo*. It is necessary thoroughly to wash the crude product prior to distillation in order to free it of aluminum compounds.

Working in accordance with the procedure outlined above, Groggins and Nagel have obtained yields of 75 to 85 per cent in the preparation of a number of alkyl aryl ketones (Table III).[1] These yields are based on both of the acyl groups in the anhydride being reactive, since it was shown previously that this was possible in the presence of 3.3 moles of aluminum chloride.

Preparation of Keto Acids.—In the preparation of benzoylbenzoic and toluylbenzoic acids which are ordinarily made on a large scale, there is a distinct economic advantage in employing the mill-type reactor, which is described and discussed on page 774. It is obvious that the cost of other types of apparatus having equal productive capacity would be greater. When, however, chlorobenzene, chlorotoluenes, etc., are condensed with phthalic anhydride, a higher reaction temperature is required, and experience has further shown that an improvement in yield and purity of keto acid is obtained when 4 to 6 moles of the halogeno compounds are employed per mole of anhydride. Condensations of this character are best carried out in a vertical-type reactor.

Liquid-phase Reactions. Preparation of 4′-Chloro-2-benzoylbenzoic Acid.—To a well-stirred mixture of 125 parts of phthalic anhydride and 600 parts of chlorobenzene at an initial temperature of about 30°C. is added 250 parts of anhydrous aluminum chloride at such a rate that the temperature of the mixture does not rise above 60 to 65°C. Some operators introduce a small amount of hydrogen chloride during the early stages of the reaction to facilitate the formation of the acid chloride and thus avoid sudden excessive pressures. After all the aluminum chloride has been added, the mixture is heated and maintained at a temperature of 75 to 80°C. for an hour or until the evolution of hydrogen chloride has substantially ceased.

In U. S. Patent 1,942,430, Jacobson shows that the aluminum chloride complex of the keto acid can be hydrolyzed in a limited quantity of cold acidulated water. Under such circumstances, only a small portion of the keto acid remains in the supernatant aromatic reactant, most of it being precipitated out in a crystalline state. Upon filtering through a wool cloth, the keto acid is separated from the rest of the charge.

Groggins and Newton obtained the results shown in Table X in the preparation of 4′-chloro-2-benzoylbenzoic acid.[2] In this investigation, the aluminum chloride complex was hydrolyzed with cold mineral acid or hydrogen chloride from an ensuing run, and the excess of chlorobenzene distilled with steam. The keto acid was then filtered off from the solution of the aluminum salt in mineral acid.

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[1] Groggins and Nagel, *Ind. Eng. Chem.*, **26**, 1313 (1934).

[2] Groggins and Newton, *Ind. Eng. Chem.*, **21**, 376 (1929).

TABLE X.—EFFECT OF CHLOROBENZENE RATIO IN AGITATED VESSELS ON PREPARATION OF 4′-CHLORO-2-BENZOYLBENZOIC ACID
Semiworks Operations[1]

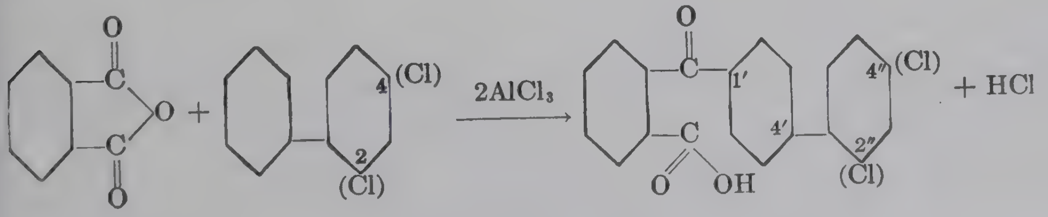
Expt. No.	Time of reaction, hr.	Temp. of reaction, °C.	Chlorobenzene ratio	Yield chlorobenzoylbenzoic acid		M. p., °C.	Purity by titration, %	Recovery of solvent, %
				Gm.	%			
1	5	50	6:1	509	97.7	147.0–148	98.8	99
2	4	50	3:1	506	97.1	147.0–148	99.6	95
3	5	50	3:1	510	98.0	147.0–148	99.6	95
4	6	40	2:1	508	97.5	147.0–148	99.6	90
5	5	95	6:1	456	87.5	147.0–147.8	98.0	
6[2]	5	50	3:1	334	64.1	144.4–147.2	98.7	

[1] Warm, dried air drawn over the reaction mass.

[2] Run without agitation.

Phthalic anhydride used, 2 moles = 296 gm.: aluminum chloride used, 587 gm. = 10 per cent excess. Sulfuric acid, 18 per cent H_2SO_4 was used in hydrolyzing the aluminum chloride complex of chlorobenzoylbenzoic acid. Of 2 per cent sodium hydroxide, 15 liters was used to form its sodium salt A 10 per cent solution of sulfuric acid was used to reprecipitate the chlorobenzoylbenzoic acid. Experiment 6 shows that agitation is necessary when a low ratio of chlorobenzene is used.

Reaction between Combining Proportions of Reactants. 4′-Phenyl-2-benzoylbenzoic Acids.—Groggins has shown that it is practical to employ the mill reactor for Friedel-Crafts syntheses involving three solid reactants.[1] When biphenyl or its halogen derivatives are condensed with phthalic anhydride, a series of 4′-phenyl-2-benzoylbenzoic acids is obtained upon hydrolysis of the aluminum chloride complex. When these keto acids are dehydrated, they are converted into phenylanthraquinones. The reactions of the chlorobiphenyls are shown by the following structural formulas:



POLYMERIZATION

Copolymerization of Isobutylene and 2, 3-Dimethyl Butadiene-1, 3.—The copolymerization of an olefin and a diolefin to produce high, rubber-like polymers is described by Thomas and Sparks as follows:[2]

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[1] GROGGINS, *Ind. Eng. Chem.*, **22**, 620 (1930).

[2] Thomas and Sparks, U. S. 2,356,130 (1944).

A mixture of 98 parts of liquid isobutylene was prepared with 2 parts of 2, 3-dimethyl butadiene-1, 3, and 2 volumes of liquid ethylene per volume were added to the mixed olefins. The mixture was prepared in a reactor equipped with a powerful stirring device and provided with a cover to avoid loss of volatilized gaseous constituents. The reactor also was well heat-insulated to reduce the rate of volatilization of the refrigerant by ambient heat. The catalyst was prepared by dissolving anhydrous aluminum chloride in methyl chloride at the boiling point of the methyl chloride to yield a saturated solution containing 1.2 per cent of aluminum chloride. This solution was then diluted with an additional amount of methyl chloride to produce a solution containing 0.6 per cent of dissolved aluminum chloride which was then precooled to a temperature slightly above the melting point of methyl chloride (−97°C.) and sprayed onto the surface of the vigorously stirred mixed olefins through a misting nozzle. The polymerization proceeded rapidly and was approximately 80 per cent complete within a few minutes.

When this stage of polymerization was reached, the polymerization mixture was diluted with approximately 0.1 volume of isopropyl alcohol to quench the catalyst and arrest polymerization. The solid polymer was then brought up to room temperature and was ready for further processing, including compounding.

The resulting interpolymer prepared from isobutylene and 2, 3-dimethyl butadiene-1, 3 was found to have a molecular weight of 110,000 and a molecular percentage of unsaturation of 1.64, as determined by iodine chloride (addition method).

The interpolymer of isobutylene and 2, 3–dimethyl butadiene–1, 3 was then compounded according to the following formula:

	Parts
Interpolymer	100
Zinc oxide	5
Stearic acid	3
Sulfur	3
Tuads	1

This prepared compound was then placed in a mold and cured at a temperature of 155°C. for 60 min. to produce the desired cured rubberlike polymer. The cured polymer was found to have a tensile strength of 3,600 lb. per sq. in. with an elongation at break of 1,100 per cent.

CHAPTER XIII

POLYMERIZATION

By W. P. Hohenstein[1] and H. Mark[1]

I. INTRODUCTION

Among the organic and inorganic substances with which the chemist and chemical engineer have to deal in either the laboratory or actual production is a group of materials that, although differing greatly in physical and mechanical behavior, show certain common properties and thus can be distinguished rather clearly from the ordinary chemical compounds. A proper characterization of a chemical compound is usually given by a number of physical and chemical properties, among which are the melting and boiling points, the molecular weight, the empirical formula, and the arrangement of the molecules in the solid state. However, such data would prove quite inadequate for characterizing this group of materials. They do not exhibit sharp melting points but rather soften gradually with increase in temperature, often passing from a hard, brittle state into a rubbery one before they finally become more or less viscous liquids. Some of these substances set permanently after the first heating and decompose on further increase in temperature. Analysis of their structure in solution and in the solid state points to the presence of well-defined chemical units of very high molecular weight. They are, therefore, usually referred to as high-molecular-weight substances or high polymers. Attempts to determine these high molecular weights by any of the conventional methods, such as freezing-point depression or boiling-point elevation, fail because of the insufficient magnitude of the effect. X-ray and electron diffraction of high polymers reveal that the molecules in some of these materials are in a state of complete disorder, whereas others exhibit a high degree of order in the arrangement of their molecules. In many cases, the diagrams indicate the simultaneous existence of ordered and disordered domains, ranging from complete disorder (amorphous state) to a high degree of order (crystalline state) of the molecular arrangement within the same material.

The very desirable mechanical, electrical, optical, and thermal properties of most of these polymeric materials led to their intensive study during the last three decades, and by now many facts are known that allow the drawing of conclusions as to formation and structure of high polymers and to the relationship between structure and physical properties.

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[1] Institute of Polymer Research, Polytechnic Institute of Brooklyn.

The outstanding fact that unites all these substances into one distinctive group is that they all consist of molecules having a very high molecular weight which ranges from about 5,000 to many millions. It is therefore understandable that the tests and methods used for ordinary, low-molecular-weight compounds cannot, in general, apply to such large molecules but that modifications and improvements had to be worked out in order to characterize high polymers properly. Many high-molecular-weight substances, such as rubber, cellulose, silk, wool, shellac, natural resins, and gums, exist in nature. Others can be produced synthetically, and, because of their industrially important properties, are at present produced in large and ever-increasing quantities.

II. PRINCIPLES OF HIGH-POLYMER CHEMISTRY

Large molecular complexes can be built up in two possible ways: either by an association of small molecules by means of *van der Waals forces* or by continuous chemical reactions between small molecules, thus establishing strong *chemical bonds* between them. In the first case, those molecular associations which exist, for instance, in water, alcohols, and organic acids are extremely sensitive to disturbances of physical or chemical nature, since the forces binding the molecules are relatively weak (3000 to 6000 cal. per mole); the dissociation energy of primary chemical bonds, however, has an entirely different order of magnitude (50,000 to 100,000 cal. per mole). Natural and synthetic high polymers consist of large molecules built up by chemical bonds of this type. Further investigation showed that in most cases, the macromolecules themselves consist of repeating low-molecular-weight units. Each single unit is called a *monomer* (monos = Greek for "one"; meros = Greek for "part"), and a macromolecule composed of many monomers is called a *polymer* (poly = Greek for "many").

The conception of ordinary organic molecules linking up to give a polymer molecule poses the question of the nature of the reaction that produces such polymers and the types of molecules that are capable of undergoing these reactions. The number of polymeric substances found in nature and produced artificially and especially the variety of properties exhibited by them seemed at first to indicate an almost unlimited number of possibilities in both respects. In later investigations, however, and primarily through the brilliant contributions of W. H. Carothers, it was shown that

1. One particular structural characteristic is common to all molecules able to participate in the formation of a polymer.
2. Essentially *two* types of reactions exist that produce very large molecules.

With the aid of these two principles, one is able to select the right kind of molecule to form a high-molecular-weight compound and, also, to synthesize new organic molecules that, when employed in one of the two types of polymerization reactions, could be expected to lead to products with valuable properties.

A. POLYFUNCTIONALITY

Carothers was the first to emphasize clearly the fact that a molecule must be *bi-* or *polyfunctional* in order to be able to take part in a reaction that produces polymers.[1,2] A molecule is called *bi-* or *polyfunctional* if two or more reactive or functional groups either are present in it at the beginning of the reaction or appear there in the course of it. Simple examples of bi- or polyfunctional molecules are hydroxy or amino acids, di- or polyalcohols, -amines, or -acids. These molecules interact with each other through their chemically active groups; but since two or more of them are located on each molecule, the reaction continues in two or three directions and linear or more dimensional molecules are formed. Figure 1 illustrates schematically the reaction between two *monofunc-*

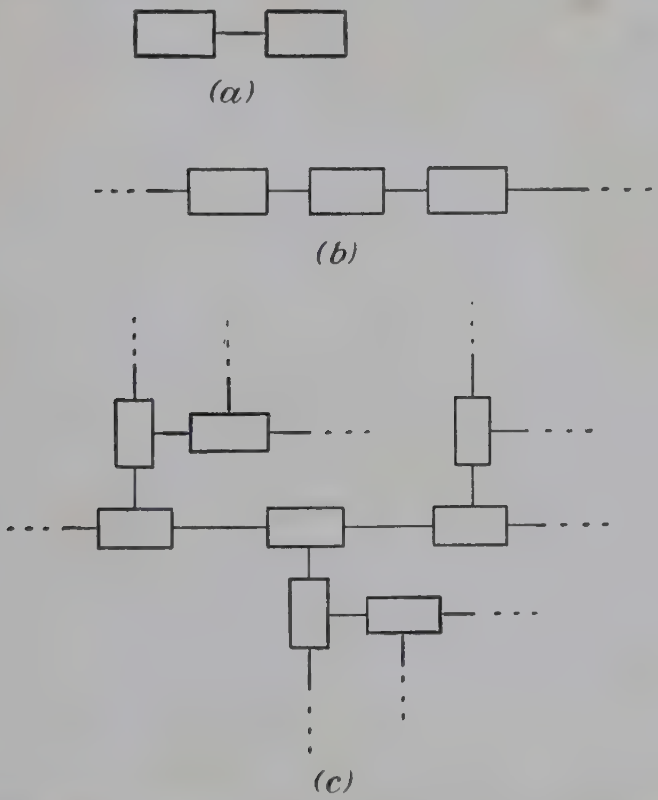

FIG. 1.—Reactions of monofunctional (*a*), bifunctional (*b*), and polyfunctional molecules (*c*).

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[1] CAROTHERS, *Chem. Rev.*, 8, 353 (1931).

[2] MARK and WHITBY; "Collected Papers of W. H. Carothers," Interscience Publishers, New York, 1940.

tional molecules, which does not produce macromolecules (*a*), whereas bifunctional monomers lead to linear chain molecules (*b*), and the reaction of trifunctional molecules produces complicated networklike structures (*c*).

Another type of bifunctionality is exhibited by a large group of of molecules containing double or triple bonds. In the polymerization of these substances, the activation of two of the electrons (second order of π electrons) of the double bond is responsible for the reactivity of the monomer on both ends. This is schematically shown in Fig. 2. Under the influence of heat, light, or a catalyst, the original symmetrical position of the two π electrons of a double bond in respect to their nuclei is disturbed, and a radical is formed. The molecule with an opened double bond then grows by collisions with other monomers (Fig. 2*a*).

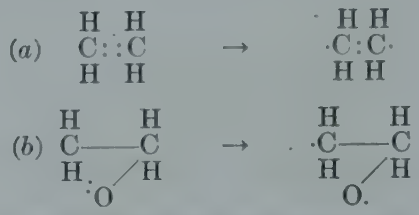


FIG. 2.—Bifunctional molecules produced by openings of double bonds (*a*) or ring structures (*b*).

Another way of producing bifunctional molecules is by the opening of three- or more-membered ring structures, as in the case of the formation of polymer molecules from ethylene oxide or tetrahydrofurane (Fig. 2*b*).

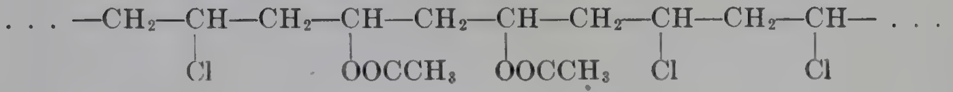
B. REACTIONS LEADING TO THE FORMATION OF POLYMER MOLECULES

There exist in principle two types of polymer producing reactions, *viz.*, *polycondensation* and *addition polymerization*. In polycondensations, bi- or polyfunctional molecules condense with one another by repeatedly splitting off H_2O, NH_3, CH_2O, NaCl, or other small molecules as the reaction proceeds. Addition polymerization, on the other hand, occurs among molecules containing double or triple bonds or bifunctional molecules resulting from the breaking of ring structures. No small molecules are liberated during this process. Polycondensations are, to the best of our present knowledge, typical step reactions, whereas the most important addition polymerizations are chain reactions. In the large molecules resulting from an addition polymerization, either the recurring low-molecular units are the monomers themselves, [formula (1)] or two or more different monomers may copolymerize. In copolymerization, the various monomers, in general, do not enter the chain according to a regular schedule but are randomly arranged throughout the length of the chain [formula (2)]:

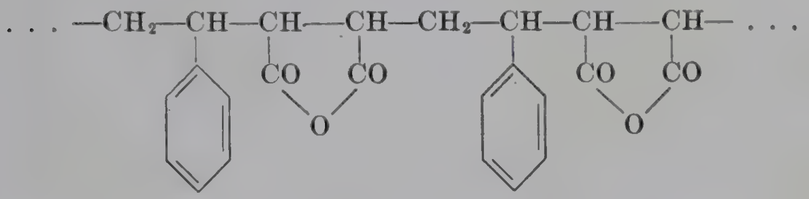
POLYMERIZATION

$$-CH_2-CH_2-CH_2-CH_2-CH_2- \qquad (1)$$

COPOLYMERIZATION

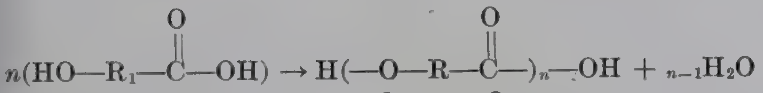


$$\ldots -CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ OOCCH_3}}{CH}-CH_2-\underset{\substack{|\\ OOCCH_3}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}- \ldots \qquad (2)$$

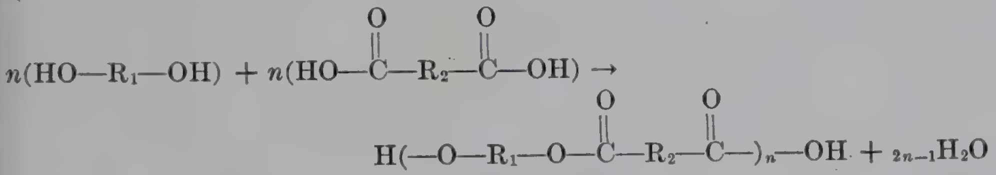


(3)

POLYCONDENSATION



$$n(HO-R_1-\overset{\substack{O\\ \|}}{C}-OH) \rightarrow H(-O-R-\overset{\substack{O\\ \|}}{C}-)_n-OH + {}_{n-1}H_2O \qquad (4)$$



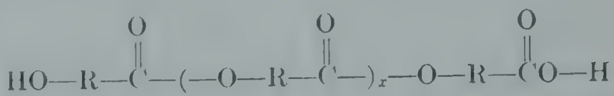
$$n(HO-R_1-OH) + n(HO-\overset{\substack{O\\ \|}}{C}-R_2-\overset{\substack{O\\ \|}}{C}-OH) \rightarrow$$
$$H(-O-R_1-O-\overset{\substack{O\\ \|}}{C}-R_2-\overset{\substack{O\\ \|}}{C}-)_n-OH + {}_{2n-1}H_2O \qquad (5)$$

Special cases of copolymerization though, for instance the one between styrene and maleic anhydride, are so-called heteropolymerizations and yield a chain polymer in which the two different monomers follow each other regularly [formula (3)]. Unlike the ordinary addition copolymers, polycondensation products generally have a regular structure as far as the sequence of the monomers in the chain is concerned, even if the recurring unit is formed by the reaction of two different bifunctional molecules with each other [formulas (4) and (5)].

1. Polycondensations

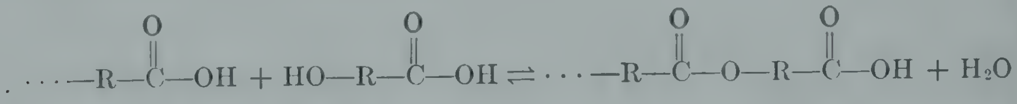
Polycondensation proceeds fundamentally in the same manner as low-molecular condensation. For instance, the energy of activation for polyesterifications is about 15,000 cal. per mole and for polyamideformation about 30,000 cal. per mole, data that come fairly close to the energy of activation for esterification and amidation of monofunctional molecules. The same acidic or basic catalysts are equally effective in the formation of both a condensation polymer molecule and a low-molecular-weight condensation product. The mechanism of the polyreaction presents all characteristics of a step reaction; *i.e.*, the chains grow proportionally to the reaction time, and each of the chain molecules is stable at any stage of the propagation process.

Polycondensations are equilibrium reactions; in order to have the reaction continue in one direction, say toward the formation of polymer chains of greater length, one has to eliminate continually the water or other volatile low-molecular-weight products of the reaction, the presence of which tends to shift the equilibrium the other way. The following example may illustrate this point. The interaction between molecules of ω-hydroxy-carboxylic acids leads to the formation of a polymer chain having the general formula



$$HO—R—\overset{O}{\overset{\|}{C}}—(—O—R—\overset{O}{\overset{\|}{C}}—)_x—O—R—\overset{O}{\overset{\|}{C}}O—H$$

in which the length of the chain is determined by the number X of —OH and —COOH groups that have reacted. The reaction itself can be characterized by the equilibrium



$$\cdots—R—\overset{O}{\overset{\|}{C}}—OH + HO—R—\overset{O}{\overset{\|}{C}}—OH \rightleftharpoons \cdots—R—\overset{O}{\overset{\|}{C}}—O—R—\overset{O}{\overset{\|}{C}}—OH + H_2O$$

If the water is not removed from the reaction mixture, further conversion of the reactants to polymer is prevented. The removal of water disturbs

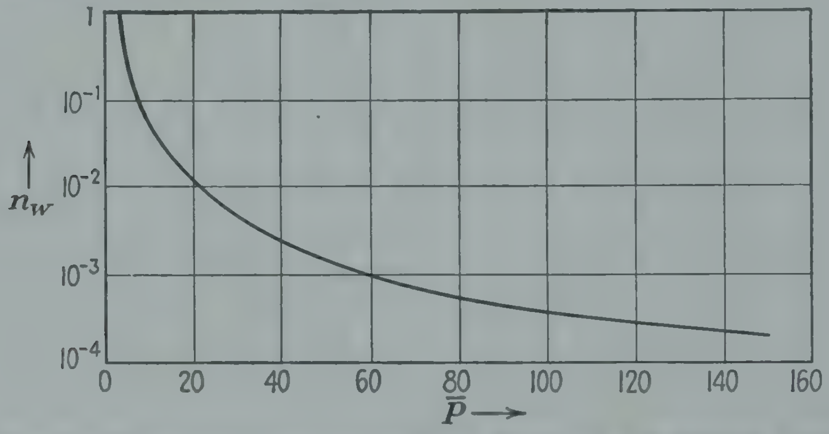
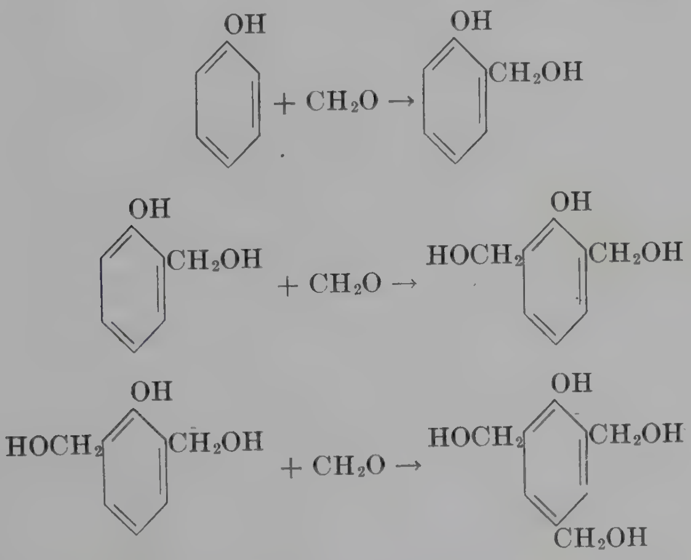


FIG. 3.—Relationship between water content (mol fractions) and average polymerization degree in polyesters.

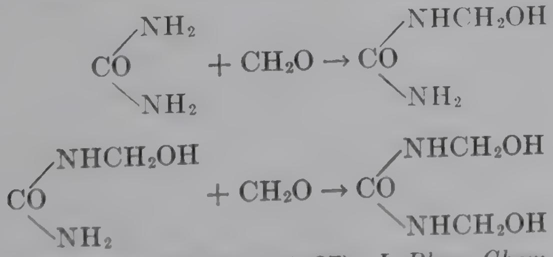
the equilibrium and favors the tendency of further chain growth. Figure 3 shows the quantitative relationship between the amount of water removed and the resulting molecular weights of some chain polymers.

The efficient elimination of the low-molecular reaction products from the reaction mixture sometimes presents a serious difficulty in the manufacturing procedure. In the later stages of the process, the viscosity of the mixture is so high that proper agitation becomes difficult and the water evolved is likely to remain trapped inside the melt. By the application of certain reaction conditions, which will be discussed later in some special cases, it is possible to overcome this obstacle and produce high-molecular-weight condensation products in large units. Although the high-melt viscosity of a polycondensation reaction mix is objectionable from the above-mentioned point of view, it has been shown recently that it does not influence significantly the rate of the reaction in its various stages.[1] This rate remains almost unchanged as the polycondensation proceeds, which seems to indicate that the reactivity of a functional group is practically independent of the length of the chains to which it is attached.

Some polycondensations are preceded by an addition reaction that first creates reactive groups in the monomer molecules. These groups, then, by polycondensation, interact with one another and form large molecules. An example is the interaction of phenol and formaldehyde in aqueous solution, resulting in the formation of mono-, di-, or trimethylol phenols, depending upon the reaction conditions, particularly upon the pH of the system. In the various products of this reaction,



the formaldehyde adds to one, two, or all three functional positions (ortho and para positions) of the phenol molecule, and a new carbon-carbon bond is established. Once the phenol alcohols are formed, polycondensation sets in, and, by splitting out water and later formaldehyde, large chain and network molecules are built up. A similar mechanism is encountered if urea and formaldehyde interact in an aqueous medium. The four functional positions on the two nitrogen atoms of urea are occupied partly or completely by methylol groups.



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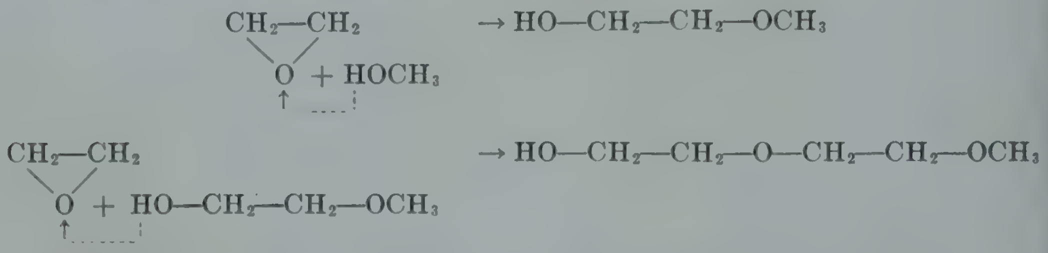
[1] Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937); *J. Phys. Chem.*, **46**, 132 (1942).

It must be emphasized that, in both cases, the products of the initial addition reaction are of low molecular weight and serve only to prepare monomeric units with two or more functional groups in the molecule.

Linear polycondensation leads to molecules with a regular succession of the monomer units along the chains; there are two functional groups at the chain ends still unreacted. In many cases, it is possible to determine the number of unreacted end groups analytically and from them to compute the number average molecular weight of the polymer.

2. Addition Polymerization

Two types of addition polymerization exist that differ in their reaction mechanism and their kinetic behavior from each other and from polycondensations. The first proceeds as a *step* reaction, whereas the second one shows all characteristics of a *chain* reaction. The step-reaction type of addition polymerization can be exemplified by the polymerization of ethylene oxide in the presence of traces of alcohol.



The chains grow proportionally to the reaction time, and each intermediate product is a stable, saturated molecule. The main difference between this reaction and a polycondensation is the absence of any reaction product that is split off during the process. On the other hand, it differs from the second type of addition polymerization in which the intermediate products are radicals of a very short average lifetime. Some addition polymers of the type discussed here have become industrially important. Foremost among them are the polymethylene oxides, polyethylene oxides, polycarbamides, and polyurethanes, which are waxy, resinous, and fibrous products.

Of particular interest, however, are those addition polymerizations which proceed as *chain* reactions. They have been investigated thoroughly from both the scientific and industrial points of view and have yielded a great variety of elastic, plastic, and fibrous materials of considerable practical value.

A chain-type addition polymerization completely differs in its mechanism and kinetics from a polycondensation. It consists of a number of separate steps which follow one another consecutively and rapidly. The intermediate products are unstable and serve only as steppingstones to the next process or product. Such reactions, therefore, produce in one sweep the final long-chain molecule once the initiating step has taken place. To the best of our present knowledge, a polymerization reaction of this type can be subdivided into the following three principal steps:

1. *The initiation or activation.*
2. *The growth or propagation.*
3. *The termination or cessation.*

Each of these individual steps of the total polymerization chain reaction has its own mechanism and kinetics; they can be represented by the following scheme:

$$\mathrm{M} \rightarrow \mathrm{M}^* \tag{1}$$

$$\mathrm{M}^* + \mathrm{M} \rightarrow \mathrm{MM}^* \tag{2}$$

$$\mathrm{MM}^* + \mathrm{M} \rightarrow \mathrm{MMM}^*$$

$$\mathrm{M}n^* \rightarrow \mathrm{M}n \tag{3}$$

First, an inactive monomer molecule M is, by some process, converted into an activated nucleus, M*, which reacts with another inactive monomer to give an activated dimer. The activity is not lost during this addition, and therefore the chain keeps on growing by adding new monomers until finally, by a termination process, the activity is destroyed and further propagation of the chain is stopped.

a. **The Initiation Reaction.**—The production of an active monomer capable of adding other monomers to form a long-chain molecule depends on a number of factors. In the first place, the energy necessary to open one of the two links of an aliphatic double bond depends upon the nature of the 2 atoms that are linked together by it, for instance, C═C, or C═O. The electronic configurations of each of these atoms and the distances between them influence the dissociation energy of the double or triple bond. In Table I, the approximate values of a number of dissociation energies of the more common types of unsaturated molecules are listed.

TABLE I.—DISSOCIATION ENERGIES OF CERTAIN BONDS

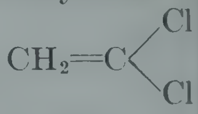
	Total Dissociation Energy Cal. Per Mole
C—C aliph	70,000
C═C aliph	100,000
C≡C	123,000
C—N	49,000
C═N	94,000
C≡N	150,000
C—O	70,000
C═O aldehyde	149,000
C═O ketone	152,000
C—S	54,000
C═S	103,000

These data show that it takes 70,000 cal. per mole to break a single bond (σ electrons, first-order electrons) between carbon and carbon atoms and only 30,000 cal. per mole more to break also the second-order (π) electrons of the double bond. If one examines the bond strengths between carbon and other atoms, such as nitrogen, sulfur, and oxygen, it becomes apparent that the dissociation energy for carbon-oxygen double bonds is comparatively high, as is the case with a carbon-nitrogen triple bond. It is known, indeed, that substances containing such bonds are very difficult to polymerize, whereas polymerization reactions involving the carbon-carbon triple bond and the carbon-nitrogen and the carbon-sulfur double bond are known.

Besides being dependent upon the nature of the atoms belonging to the double or triple bond, the energy required to activate the bond is influenced by two more factors:

1. By substituents on one or both sides of the multiple bond.
2. By the presence of conjugated or cumulated multiple bonds.

It can be generally stated that substitution decreases the energy necessary for activation of the bond and especially so if it is unsymmetric, *i.e.*, if one or both hydrogen atoms on only one carbon atom of the double bond are replaced. If substitution in the vicinity of the double bond becomes too heavy, the tendency to polymerize decreases rapidly, presumably because of steric hindrance or resonance stabilization. Also of importance for the reactivity of the double bond is the nature of the substituents. The following examples illustrate these empirical rules.

Ethylene, $CH_2{=}CH_2$, polymerizes only under high pressure (about several hundred atmospheres) and high temperatures (250°C. and above), whereas most of the monosubstituted ethylenes, the so-called vinyl derivatives, $CH_2{=}CHX$, polymerize under very much milder conditions. Only if the substituent is very bulky, such as in vinylanthracene or vinyl fluorene, a decrease in the tendency to polymerize can be observed. If the number of substituents is raised to two, it turns out that asymmetrically substituted monomers, such as vinylidene chloride,  $CH_2{=}C\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown Cl}$ polymerize much more easily than symmetrically substituted compounds, such as 1, 2-dichloro-ethylene, $ClHC{=}CHCl$. Further increase in the number of substituents leads to virtually unpolymerizable products, as, for instance, trichloroethylene, $Cl_2C{=}CHCl$. Examples of the influence of the *nature* of the substituent on the ease of polymerization are propylene and vinyl chloride. Propylene is very much more difficult to polymerize than vinyl chloride, which might be attributed to the polar nature of the chlorine.

As far as conjugated and cumulated systems are concerned, it has been generally found that the ease of polymerization increases with the amount of unsaturation and that conjugation or cumulation of double bonds increases their reactivity. To support this general rule, Table II shows a comparison of the rates of polymerization of hydrocarbons that differ only in their unsaturation.[1]

TABLE II.—COMPARISON OF THE RATES OF POLYMERIZATION OF HYDROCARBONS DIFFERING ONLY IN THE AMOUNT OF UNSATURATION, ACCORDING TO H. E. THOMSON

Compound	% Conversion under Given Conditions
Butene-1, $CH_2{=}CH{-}CH_2{-}CH_3$.	39.6% in 52.5 sec. at 750°C. Stable at 200°C.
Butadiene-1, 3, $CH_2{=}CH{-}CH{=}CH_2$.	10 days at 150°C. in sealed tube, "all" polymerized. 70% polymerized in 1 hr. at 350°C.
Vinylacetylene, $CH{\equiv}C{-}CH{=}CH_2$. . .	Explosive polymerization on contact with sulfuric acid or upon heating. Under pressure readily polymerized to a solid. Homologues form viscous sirups upon standing for 2 or 3 months

Whereas Table II shows the influence of the amount of unsaturation Table III indicates the importance of the relative position of the double and triple bonds on the tendency of a molecule to polymerize.[2]

TABLE III.—INFLUENCE OF CONJUGATION ON POLYMERIZATION

Substance	Formula	Polymerization
Diacetylene.	$CH{\equiv}C{-}C{\equiv}CH$	Polymerizes extremely rapidly
Divinylacetylene. . .	$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$	Polymerizes rapidly
Vinylacetylene.	$CH{\equiv}C{-}CH{=}CH_2$	Polymerizes very readily
Butadiene-1, 3.	$CH_2{=}CH{-}CH{=}CH_2$	Polymerizes readily
Pentadiene-1, 4. . . .	$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$	Rearranges into the conjugated system and polymerizes readily
Hexadiene-1, 5.	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$	Polymerizes slowly

Other interesting relationships exist for double bonds located in five- or six-membered rings. Cyclopentadiene can be readily polymerized, and combinations of five- and six-membered rings containing conjugated double bonds, such as coumarone and indene, exhibit a strong tendency to polymerize.

It must be pointed out that outside the energy requirement for the activation of a double or triple bond, a number of other factors are responsible for the success or failure of a polymerization reaction. Important are, for instance, the stability of the radical that is formed by opening one link of the double bond, also the steric configuration of the monomer. If the circumstances are unfavorable for the formation of large molecules, then very drastic reaction conditions must be employed to promote polymerization, even if all energy requirements are fulfilled.

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[1] THOMPSON in BURK, THOMPSON, WEITH, and WILLIAMS, "Polymerization," p. 16, Reinhold Publishing Corporation, New York, 1937.

[2] MARK and RAFF, "Highpolymer Reactions," Interscience Publishers, New York, 1941.

The energy for the activation of the double bond can be supplied in the form of heat or by irradiation, preferably with ultraviolet light; and as in almost any other chemical process, a considerable increase in rate can be obtained by the use of a catalyst. Therefore, one distinguishes among

1. Thermal polymerization.
2. Photo polymerization.
3. Catalytic polymerization.

It is extremely difficult to perform a pure thermal polymerization, since traces of air or impurities of the monomer may already have a catalytic effect on the reaction. Some investigators have measured thermal polymerizations with great precaution and have calculated the energy of activation of the initiation reaction for styrene, vinyl acetate, and methyl methacrylate. Their results are summarized in Table IV.[1,2]

TABLE IV.—CALCULATED ENERGY OF ACTIVATION FOR INITIATION OF SOME POLYMERIZATIONS

Compound	Temp. range, °C.	Activation energy, cal. per mole
Styrene	79.5–131.5	23,500
Vinyl acetate	81.8–110.9	23,100
Vinyl acetate in toluene	81.8–110.2	22,300
Methyl methacrylate	100–210	10,300

Photopolymerization of acrylic esters in the gaseous phase was studied by M. W. Melville, who observed that once some molecules of methyl methacrylate had been activated by ultraviolet light, the growth of the chains proceeded slowly in the dark and continued even if the growth process had been interrupted by temporary evacuation of the reaction vessel.[3]

Most of the theoretically and practically important polymerization reactions are carried out in the presence of catalysts, and most of the studies have been concentrated on this type of reaction. It has been found that the polymerization of olefins and diolefins can be greatly accelerated by the use of one of two types of catalysts, each of which is

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[1] For further reference see Mark and Raff, "Highpolymer Reactions," Interscience Publishers, New York, 1941.

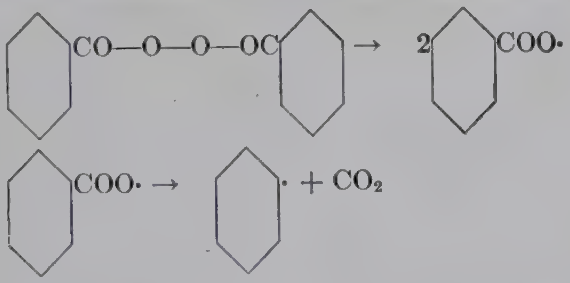
[2] SCHULZ and HUSEMANN, *Z. physik. Chem.* (B) **34,** 187 (1936).

[3] MELVILLE, *Proc. Royal Soc.* (*London*), **163,** 511 (1934).

efficient for special polymerization conditions. The two types are usually designated as

1. Radical-type catalysts.
2. Ionic-type catalysts.

It is not surprising that a reaction proceeding through the formation of radicals should be accelerated by substances that, under the reaction conditions, form radicals themselves. A large number of such substances are known, but the most widely used are organic and inorganic peroxides and salts of peracids. Among those, benzoyl peroxide and acetyl peroxide give best results as hydrocarbon-soluble catalysts, and hydrogen peroxide, potassium perborate, or potassium persulfate as water-soluble catalysts. Particularly, the effect of benzoyl peroxide on the initiation reaction has been carefully investigated, and certain conclusions can be drawn as to the mechanism of that reaction. Benzoyl peroxide, under the influence of heat, splits into radicals according to the following scheme:[1,2]



The benzoyl or phenyl radicals collide with monomer molecules and thereby produce the active centers for the start of a polymer chain.

Recent investigations, however, have shown that the initiation reaction is of a somewhat more complex nature.[3,4,5] In order to fit the experimental data, it seems necessary to assume that benzoyl peroxide and the monomer form first a molecular addition product, which is then converted into the active center.

It is now generally assumed that remnants of the catalyst are permanently attached to the first link of the polymer chains. This view has been substantiated by experiments showing that fragments of halogenated benzoyl peroxide or other catalysts can be found even in the most thoroughly purified polymers.[6,7,8,9,10]

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[1] McCluve, Robertson, and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

[2] Nozavi and Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

[3] Schulz, Blaschke, and Dinglinger, *J. prakt. Chem.*, **158**, 130, 136 (1941).

[4] Schulz and Husemann, *Z. physik. Chem.* (B) **52**, 1, 23, 50 (1941).

[5] Josefowitz and Mark, *Polymer Bull.* I, 140 (1945).

[6] Pfann, Salley, and Mark, *J. Am. Chem. Soc.*, **66**, 983 (1944).

[7] Price, Kell, and Krebs, *J. Am. Chem. Soc.*, **64**, 1103 (1942).

[8] Price and Tate, *J. Am. Chem. Soc.*, **65**, 517 (1943).

[9] Price and Durham, *J. Am. Chem. Soc.*, **64**, 2508 (1942).

[10] Bartlett and Altschul, *J. Am. Chem. Soc.*, **67**, 812, 816 (1945).

The catalytic action of highly polar molecules on a polymerization is a well-established empirical fact, but not much is known about the mechanisms of this kind of catalysis. The addition of dipoles such as boron trifluoride, aluminum chloride, or tin tetrachloride accelerates the polymerization under certain conditions and is especially effective on asymmetrically di-substituted vinyl derivatives. For instance, isobutylene can be polymerized at a temperature of −70°C. by employing small amounts of boron trifluoride; because of the low temperature, very high molecular weights are obtained.

As a possible mechanism of this reaction, it is suggested that as the dipole molecule approaches the monomer to a distance where coulombic forces become effective, the electrical symmetry of the double bond is disturbed and the second-order electrons are either attracted or repelled. A catalyst-monomer complex is formed, which has the character of a dipole itself and acts as such on the next approaching monomer. This process repeats itself until a long-chain molecule is formed. It seems that somehow during the course of the reaction either the original dipole detaches itself and the whole chain molecule reverts to an unpolar state again or a proton is split off at the last link, whereby a similar depolarization of the chain is effected.

b. **The Propagation Reaction.**—Once a monomer has been activated, it is able to react with another inactive monomer in an exothermic reaction step. The activation energy of this process has been found to be between 6,000 and 12,000 cal. per mole, and consequently many collisions between activated chain ends and inactive monomers are successful. Hence, the sequence of additions is very rapid.

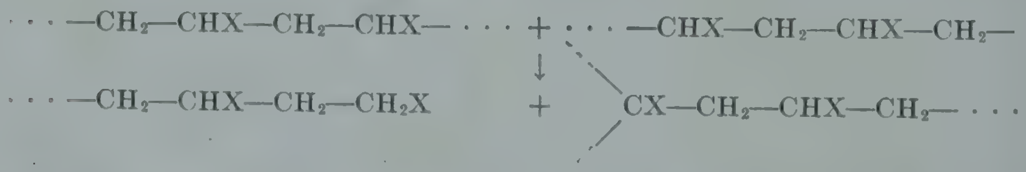
$$\begin{gathered} M^* + M \rightarrow MM^* \\ MM^* + M \rightarrow MMM^* \end{gathered}$$

Chain propagation can occur according to one of three possible schemes:

1. The chains grow normally by continuous addition of new monomer units until a termination reaction stops further propagation:

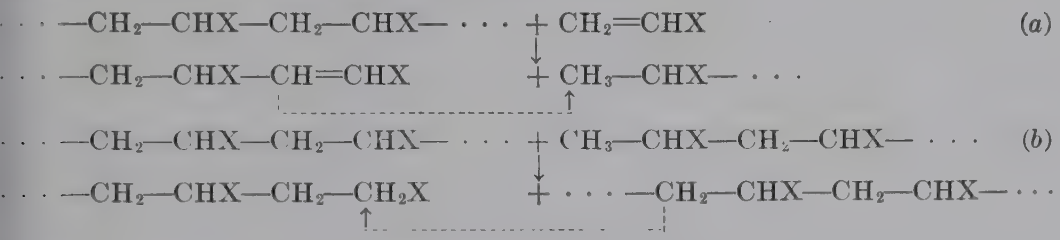
$$\cdots\text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}CHX\text{—}\cdots$$

2. A collision between two chains causes the formation of a branched chain:


$\cdots\text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}CHX\text{—}\cdots + \cdots\text{—}CHX\text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}$
$\cdots\text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}CH_2X + CX\text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}\cdots$

This process seems to be favored at high conversions and elevated temperatures.

3. On collision of a growing chain with either a monomer or an already completed chain, chain transfer may take place:



$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots + \text{CH}_2\text{=CHX} \qquad (a)$$
$$\downarrow$$
$$\cdots\text{—CH}_2\text{—CHX—CH=CHX} + \text{CH}_3\text{—CHX—}\cdots$$

$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots + \text{CH}_3\text{—CHX—CH}_2\text{—CHX—}\cdots \qquad (b)$$
$$\downarrow$$
$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CH}_2\text{X} + \cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots$$

In the first case (*a*), the growing chain is closed by the formation of a double bond, and the now activated monomer starts a new chain. If a growing chain collides with a closed chain (*b*), it sometimes happens that an H atom is picked up, which terminates the growing chain, leaving a free valence on the previously closed end of the other one. It must be pointed out that, in both reactions of branching and chain transfer, the number of active centers does not change, because each instance of chain termination is accompanied by the creation of a new active center.

Experiments indicate the presence of straight and branched chains in materials derived from the same monomer. Kinetic considerations and a decrease in average molecular weight as compared with the normally expected one point to the occurrence of chain-transfer processes. It must therefore be assumed that all three types of chain propagation can occur simultaneously.

The mode of addition of a substituted ethylene monomer during the propagation reaction leads to different arrangements of the substituents along the chains. According to C. S. Marvel, the monomers can add in a "head-to-tail" or "head-to-head" arrangement.[1] It has been experimentally demonstrated that, in most polymerizations and copolymerizations, the head to-tail addition is preferentially maintained throughout the polymer molecules; some evidence points to a head-to-head configuration in a few cases.

$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots$$

Head-to-tail arrangement

$$\cdots\text{—CH}_2\text{—CHX—CHX—CH}_2\text{—}\cdots$$

Head-to-head arrangement

c. **The Termination Reaction.**—The most common termination or cessation processes are

1) The collision between two growing chains.

2) The collision of a growing chain with a catalyst radical.

3) The collision of a growing chain with impurities or walls of the reaction vessel.

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[1] Marvel, "Frontiers of Chemistry," Vol. I, p. 219, Interscience Publishers, New York, 1943.

The effect of a collision between two growing chains can be twofold: either the two free valences unite to a single bond in a coupling reaction

$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots + \cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots$$
$$\downarrow$$
$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots$$

or a disproportionation of the two colliding chain molecules takes place

$$\cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots + \cdots\text{—CH}_2\text{—CHX—CH}_2\text{—CHX—}\cdots$$
$$\downarrow$$
$$\cdots\text{—CH}_2\text{—CHX—CH=CHX} + \text{CH}_3\text{—CHX—CH}_2\text{—CHX—}\cdots$$

producing an unsaturated and a saturated terminal link on the two chains, respectively. The first possibility tends to increase the average molecular weight, since by the coupling of two chains one large molecule is formed, whereas disproportionation leads to products of lower average molecular weight.

The probability of collisions between activated chain ends and catalyst fragments increases proportionally to the concentration of the catalyst in the system. Whereas a high catalyst concentration effectively accelerates the polymerization by producing a comparatively large number of active centers, it provides, on the other hand, for chain breakers and prevents the development of long chains. In practice, therefore, some speed of polymerization has to be sacrificed if high-molecular-weight material is desired, and the catalyst concentration must be kept within limits.

The fact that active centers lose their activity upon collision with certain molecules has been industrially exploited in cases where polymerization of a given monomer is undesirable at a certain time. The production of the monomer itself often involves distillations or other operations at elevated temperatures during which polymerization must be avoided. Storing and shipping monomers are other occasions when they must be kept stable for a considerable length of time. This is achieved by deliberately adding, to the monomer, small amounts of so-called *inhibitors*, the function of which is to stop any chain growth, preferably immediately after the initiation has occurred. Very effective inhibitors, among others, are substances containing quinoid, nitro, amino, or phenolic hydroxyl groups. They must be removed by adequate washing or distilling operations before the monomer is subjected to polymerization. Frequently it is difficult to free a monomer of all inhibiting influences, which in some circumstances may even be traces of oxygen. Thus, practically all polymerization reactions begin with a period in which the formation of large molecules is either completely impeded or at least retarded. This phase of the reaction is known as the *inhibition period*, and only relatively low-molecular-weight products are formed in it. It is obvious that a prolongation of the inhibition period has as a consequence a lowering of the average molecular weight of the final polymer. A thorough purification of the monomer before polymerization is, therefore, indicated if high-molecular-weight material is desired.

III. CHARACTERIZATION OF HIGH POLYMERS

To characterize a given high-polymer sample, it is necessary to describe properly first the molecules themselves and then the way in which they are arranged in respect to one another. The knowledge of the molecular structure of a given polymer makes it possible to understand and, in some cases, even to predict to a certain degree its mechanical, optical, and electrical properties.

Ordinary organic substances are first characterized by their empirical formula and their molecular weight. The next step is to establish the presence of certain characteristic groups, and the final goal is to write down a three-dimensional structural formula, which completely locates all atoms and expresses their mutual relationships (single, double, triple bonds, etc.). In the case of high polymers, it has been found that most samples are not homogeneous, in that they contain molecules of the same structural formula but of different molecular weights. One is therefore faced with the necessity of considering a high-polymeric material as a more or less heterogeneous mixture of long-chain molecules that have essentially the same chemical composition. Under these conditions, two questions present themselves:

1. What is the average molecular weight of the material?
2. Which is the shape of the molecular-weight distribution curve?

The Molecular-weight Averages

As to the *average molecular weight* or *polymerization degree*, it is necessary to point out that different average values of a given distribution curve exist.[1,2,3]

1. The *number-average* molecular weight $\overline{M_n}$ or *number-average degree of polymerization* $\overline{DP_n}$, which are defined by the equations

$$\overline{M_n} = \frac{\Sigma n_i M_i}{\Sigma n_i} \tag{1}$$

$$\overline{DP_n} = \frac{\Sigma n_i DP_i}{\Sigma n_i} \tag{2}$$

where n_i is the number of molecules belonging to the i^{th} species, whereas

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[1] Mark and Raff, in "High Polymeric Reactions," High Polymer Series, Vol. III, p. 47, Interscience Publishers, New York, 1941.

[2] Lansing and Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).

[3] Schulz, *Z. physik. Chem.*, **B30**, 379 (1935); **B40**, 466 (1938); **B43**, 47 (1939).

$\overline{M}_i$ and $\overline{DP}_i$ are the corresponding molecular weights and degrees of polymerization. These number averages can be determined by osmotic measurements or by the analytical determination of end groups.

2. The *weight-average* molecular weight $\overline{M}_w$ or *weight-average degree of polymerization* $\overline{DP}_w$, which are defined by the relations

$$\overline{M_w} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} \tag{3}$$

$$\overline{DP_w} = \frac{\Sigma n_i DP_i^2}{\Sigma n_i DP_i} \tag{4}$$

can always be determined by light-scattering measurements,[1] under certain conditions also by viscosity measurements,[2,3] and by sedimentation and diffusion measurements. In general the last methods, however, lead to more complicated averages.[4]

3. The so-called *z-average molecular weight* $\overline{M}_z$ and *z-average degree of polymerization* $\overline{DP}_z$, which are given by

$$\overline{M}_z = \frac{RT\, ln \dfrac{c_1}{c_2}}{(1 - V_\rho)\omega^2(x_2^2 - x_1^2)} \tag{5}$$

$$\overline{DP}_z = \frac{\overline{M}_z}{M_0} \tag{6}$$

where c_1, c_2, are concentrations at x_1, x_2, respectively, V is the specific volume of the dry polymer, and ρ represents the density of the solvents.

The sharper the distribution curve of a given sample the nearer together fall the above-mentioned average values; in a very homogeneous sample they coincide. In normal natural and commercial synthetic high polymers, the ratio between the weight and number average is not smaller than 1.5 and not larger than 2.5, whereas the z averages usually are about 2.5 to 4.0 times larger than the number averages.

Osmotic measurements,[5] are usually carried out in osmotic cells made of glass or stainless steel; they give fairly reliable results in the molecular-weight range from 5,000 to 500,000 and are evaluated with the aid of the equation

$$\frac{\pi}{c} = \frac{RT}{M} + \frac{RT}{V_1 d^2}\left(\frac{1}{2} - \mu\right) c = RT\left(\frac{1}{M} + Bc\right) \tag{7}$$

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[1] DOTY, ZIMM, and MARK, *J. Chem. Phys.*, **13**, 159 (1945).

[2] HUGGINS, in E. OTT, "Cellulose and Cellulose Derivatives," High Polymer Series, Vol. V, p. 943, Interscience Publishers, New York, 1943.

[3] PFEIFFER and OSBORN, in E. OTT, "Cellulose and Cellulose Derivatives," Vol. V, High Polymer Series, p. 956, Interscience Publishers, New York, 1943.

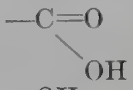
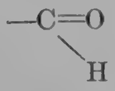
[4] KRAEMER and NICHOLS, in SVEDBERG and PEDERSON, "The Ultracentrifuge," p. 418, Clarendon Press, Oxford, 1940.

[5] SPURLIN, in E. OTT, "Cellulose and Cellulose Derivatives," High Polymer Series, Vol. V, p. 910, Interscience Publishers, New York, 1943.

π in this equation represents the osmotic pressure, R and T the gas constant and absolute temperature respectively, M the (number average) molecular weight, c the concentration of the polymer, V_1 the molar volume of the solvent, and d the density of the polymer. μ is a constant that characterizes the interaction of the solvent with the individual segments of the dissolved macromolecule.[1,2]

The *end groups* that are most frequently found in high polymers are carboxyl, hydroxyl, amino, and aldehyde groups. Table V summarizes methods by which these groups can be determined quantitatively.

TABLE V.—METHODS OF DETERMINING END GROUPS

 $-C{=}O$, $\backslash OH$	*a.* Titration *b.* Ag salt
$-OH$	*a.* Methylation (Zeisel) *b.* Active H (Zerewittinoff)
$-NH_2$	Diazonium salt (Van Slyke)
 $-C{=}O$, $\backslash H$	*a.* Oxidation to carboxyl *b.* Fehling solution *c.* Dimethyl dehydro resorcinol
$-CH{=}CH_2$	*a.* Ozonolysis *b.* Addition to halogen (Vijs, Marshall) *c.* Nitrosobenzene *d.* Thiocyanogene

Light-scattering measurements are carried out either visually or photometrically by scattering a parallel, monochromatic beam of visible light under an angle between 30 and 150 deg.; they are evaluated by the equation[3]

$$\frac{c}{\tau} = \frac{1}{H}\left[\frac{1}{M_2} + \frac{2B}{RT}c + \cdots\right] \tag{8}$$

where τ is the *turbidity* of the solution; H is a constant depending upon the wave length of the scattered light and upon the refractive indices of the solvent and the solution; R, T, and B have the same meaning as in Eq. (7); and M is the weight-average molecular weight of the sample.

Sedimentation measurements are carried out in the Svedberg Ultracentrifuge by sedimentation velocity runs, and *diffusion* experiments are performed in one of the conventional diffusion cells. In the analysis of high-polymer samples, both the sedimentation and diffusion constants are extrapolated to infinite dilution, and then the molecular weight M is determined by the Svedberg equation

$$\overline{M}_w = \frac{RTs}{D(1 - V_\rho)} \tag{9}$$

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[1] HUGGINS, *J. Am. Chem. Soc.*, **64**, 1712 (1942).

[2] FLORY, *J. Chem. Phys.*, **9**, 660 (1941).

[3] DEBYE, *J. Appl. Phys.*, **15**, 338 (1944).

where s and D are the sedimentation and diffusion constants extrapolated to zero concentration, R and T have their usual meaning, V is the specific volume of the dry polymer, and ρ the density of the solvent.

The *z-average molecular weight* is obtained by sedimentation equilibrium experiments in the ultracentrifuge.

The above methods are absolute determinations of the molecular weight of dissolved polymers, because the equations on which they are based do not contain any empirical constants but only such magnitudes (R, T, V, ρ, H, etc.) as can be measured in absolute values by independent experiments. The determination of the molecular weight of a polymer by *viscosity*, however, needs calibration by one of the above absolute methods. The viscosity of the polymer solution η_c and the viscosity of the solvent η_0 are usually measured by the capillary method. Then the so-called *specific viscosity* (η_{sp})

$$\eta_{sp} = \frac{\eta_c - \eta_0}{\eta_0}$$

is computed. Experience has shown that, in the range of very dilute solutions, a straight line is obtained if one plots $\eta_{sp/c}$ versus c. Huggins has represented this fact by the equation[1]

$$\frac{\eta_{sp}}{c} = \eta_i + \eta_i^2 \cdot k'c \qquad (10)$$

where c is the concentration, usually expressed in grams of solute per 100 cc. of solvent, whereas η_i and k' are constants. The value of η_i, the so-called *intrinsic viscosity* $[\eta_i]$, can be obtained as the intercept on the ordinate in a plot of Eq. (10). It was found that this intrinsic viscosity is connected with the molecular weight of the dissolved polymer by an equation of the form

$$\eta_i = KM^a \qquad (11)$$

where K and a are constants. In some cases, it has been found that the value of a is unity or very nearly so, which involves direct proportionality between intrinsic viscosity and molecular weight as demanded by the Staudinger rule. Under these conditions, the viscosity method gives the weight-average molecular weight, whereas for values of a, smaller or larger than unity, Eq. (11) leads to a more complicated average value.[1]

THE DISTRIBUTION FUNCTION

A more thorough characterization of a high-polymer sample than its average molecular weight is obtained by indicating the proportions of the various molecular sizes in the material. Such distribution functions define either the *number fraction* of molecules having molecular weights within a certain range, *i.e.*, between a molecular weight of 50,000 and 55,000, or the *weight fraction* of this particular molecular-weight range. They are consequently called *number-* and *weight-distribution curves* and differ in significance and shape from each other. There are two methods to arrive at such distribution functions:

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[1] HUGGINS, *J. Am. Chem. Soc.*, **64**, 1712 (1942).

1. The analytical determination of the spread of the distribution curve without actually separating the fractions. This can best be done in the ultracentrifuge.[1] Recently it was also attempted to arrive at analytical distribution functions from light scattering.[2]

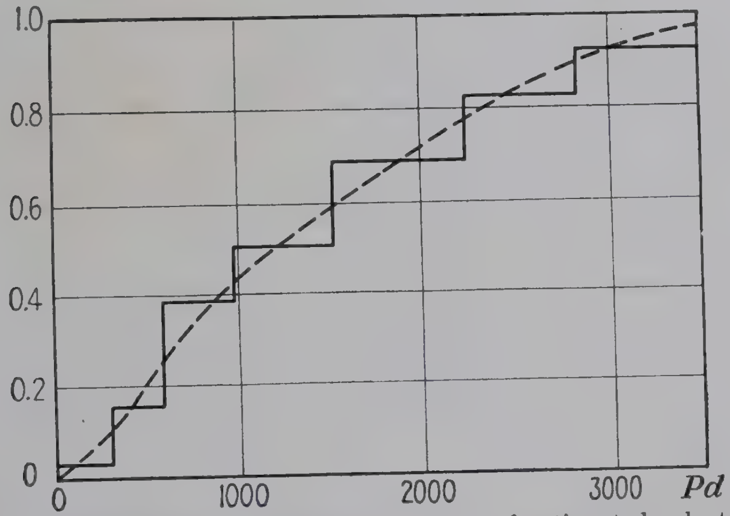

FIG. 4.—Integral weight-distribution curve of a fractionated polystyrene.

2. The actual resolution of a given polymer into a number of fractions the weight and molecular weight of which can be determined.

Actual fractionation of polymers is carried out by either fractionated solution or fractionated precipitation. If one adds a precipitant to a dilute solution of a polymer, the highest molecular-weight fraction comes down first; subsequently, lower ones can be secured until finally the lowest molecular-weight fractions can be obtained by evaporating the solvent. Repeated refractionation increases the number of fractions and decreases the heterogeneous character of the molecular species contained in them. The molecular weights of the fractions, obtained by any of the above-mentioned methods, can then be used to draw, first, a step curve which can be interpolated by a continuous curve (Fig. 4). The accuracy of this interpolation obviously depends upon the number of experimental fractions available for the construction of the step curve. By graphical differentiation of this *integral* distribution curve, *differential* distribution curves (Fig. 5) are obtained, which offer a highly descriptive picture of the relative frequency of the various molecular species in the polymer. Such distribution curves have recently received considerable attention in industry because they allow a very rigorous standardization of polymers and permit in a very similar way the discovery of slight aberrations and changes during the large-scale production of polymers. As an example, the degradation of cellulose may be cited, as it occurs during the various pulping processes. Since the properties of the resulting cellulose are greatly dependent on the proportions of low-molecular fraction, the processes are adjusted to the requirements of the various industrial applications of the cellulose and controlled by distribution-curve analysis.

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[1] KRAEMER, *et al., loc. cit.*

[2] ZIMM and DOTY, *J. Chem. Phys.*, **12**, 203 (1944).

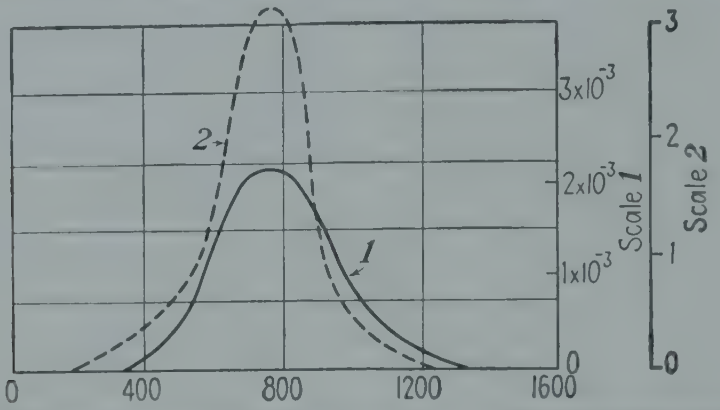

Fig. 5.—Differential weight-distribution curve of a fractionated polystyrene.

Structure of the High-polymer Chain

With the aid of organic chemical methods, it has been shown that, in many cases, monomers of the vinyl type enter a growing chain preferentially in the head-to-tail position.[1] This had been found to be true also in copolymerizations of two or more different monomers,

$$\cdots —CH_2—CHX—CH_2—CHY— \cdots$$

though, in such reactions, the sequence of the monomers X and Y is almost never regular. This fact accounts for the difficulty of a complete structural analysis of copolymers. In most cases, one knows only the relative amounts of the different monomers that contribute to the chain formation. In some cases, however, it has been possible to obtain a more detailed structural formula by the analysis of the products of a careful ozonolytic scission of the polymer.[2,3] Dienes are also able to influence the structure of a polymer molecule, since they may add either in a 1, 4, position

$$CH_2{=}CH—CH{=}CH_2 \rightarrow \cdots —CH_2—CH{=}CH—CH_2— \cdots$$

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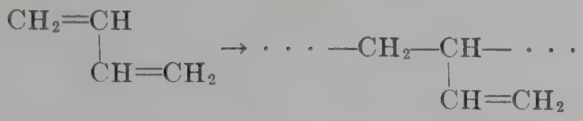
[1] Marvel, *loc. cit.*

[2] Rehner, *Ind. Eng. Chem.*, **36**, 46 (1944).

[3] Kamenskaya and Medvedev, *Acta Physico chim. U.S.S.R.* **13**, 565 (1940).

or in a 1, 2, position



$$\begin{matrix} CH_2{=}CH \\ | \\ CH{=}CH_2 \end{matrix} \rightarrow \cdots -CH_2-\underset{\begin{matrix} | \\ CH{=}CH_2 \end{matrix}}{CH}- \cdots$$

The amount of 1, 2 addition can be determined by ozonolysis of the residual double bond to formaldehyde and subsequent oxidation to formic acid.[1]

The use of X-ray and electron diffraction has also largely contributed to our knowledge of the fine-structure of many polymers. The interpretation of diffraction diagrams of some polymers allows the drawing of certain conclusions as to the geometrical structure of the chain and to the probable positions of the substituting atoms in respect to the main carbon-carbon chain. Thus it has been established that polyethylene chains inside crystalline regions have a regular zigzag structure and that the C atoms all lie in one plane (Fig. 6). In many other cases, the diffraction methods have also been capable of contributing very valuable information to the spacial configuration of the chain molecules.[2,3,4]

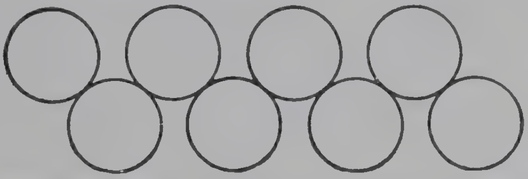


FIG. 6.—Scheme of a polyethylene chain; zigzag configuration in one plane.

TECHNICAL TESTS

Besides characterizing a high-polymeric material by a description of its molecules and its molecular arrangement, the material itself can be subjected to a variety of *mechanical*, *thermal*, *permanence*, *optical*, and *electrical* tests, which describe its properties in these respects. Because the choice of a polymer for any specific application is largely based on its particular properties, the trade in conjunction with the ASTM have established standards by which polymers can be compared with one another and with other working materials. The most important among them are

1. **Thermal and Chemical Tests.**—Solubility in various solvents, water absorption, softening range, and cold flow.

2. **Permanence Tests.**—Corrosion resistance, weather resistance, oil resistance, resistance to chemical agents, heat and light degradation, and aging.

3. **Mechanical Tests.**—Impact strength, tensile strength, elongation and hysteresis, creep and recovery, flexibility and foldability, mold shrinkage, and heat distortion.

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[1] KAMENSKAYA and MEDVEDEV, *Acta Physico chim. U.S.S.R*, **13,** 565 (1940).

[2] BAKER, FULLER, and PAPE, *J. Am. Chem. Soc.*, **64,** 776, 2399 (1942).

[3] BAKER and FULLER, *Ann. N. Y. Acad. Sci.*, **44,** 329 (1943).

[4] MARK, *Ind. Eng. Chem.*, **34,** 449, 1343 (1942).

4. Optical Tests.—Refractive index, light transmission, color range, scattering, and light fastness.

5. Electrical Tests.—Dielectric constant, dielectric strength, volume resistivity, power loss, and power factor.

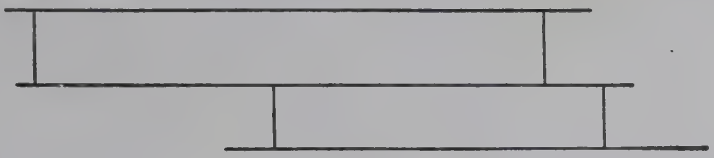
A number of specific tests have been devised for the application of polymers for special purposes, such as damping tests for frequency modulations of short or long waves or scratch resistance on protective coatings, etc.

IV. RELATION OF SIZE AND SHAPE OF THE POLYMER MOLECULE TO ITS PHYSICAL AND MECHANICAL BEHAVIOR

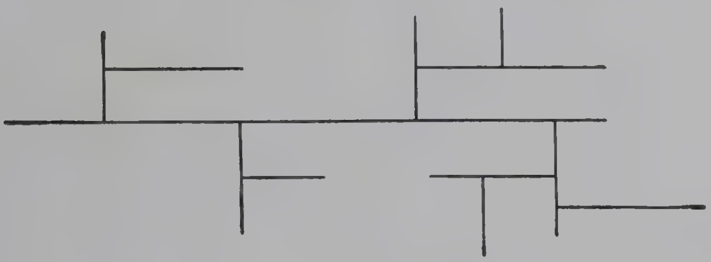
The chemical nature of the monomer, the average molecular weight, the distribution function, and the sequence of the monomer units in the polymer molecule (linear or three-dimensional) determine the thermal and mechanical behavior of the material. Extensive experience indicates that polymers consisting of linear-chain molecules are always soluble, even if the molecular weight is very high, and are thermoplastic. Three-dimensional molecules are insoluble in any kind of solvent and are thermosetting. *Thermoplastic* resins soften on heating and become rigid again on cooling; they can be melt-cast, injection molded, extruded, and melt-spun. The process of heat-softening, forming, and cooling can be repeated as often as necessary and does not bring about appreciable changes in the appearance or properties of the polymer. A *thermosetting* material, however, can be heat-treated only once before it has set, after which further heating results only in chemical decomposition. Thus, thermoplastic or thermosetting behavior of a material is directly connected with the structural details of its molecules and can be changed at will. Cross-linking agents can artifically create three-dimensional networks from straight chains and thereby convert a thermoplastic material into a thermosetting one. The vulcanization of rubber is the most spectacular example of such a process. The change from a thermosetting to a thermoplastic polymer is performed by the opening of strong cross links and is, for instance, commercially carried out on a large scale in the reclaiming of rubber.

The solubility characteristics of a polymer are very sensitive to cross linking, even more so than the thermal behavior. Even slight cross linking (insufficient to cause infusibility) may render a polymer insoluble. Less drastic is the influence of branching on the solubility of a polymer; it usually decreases the rate of solution but does not make a material completely insoluble (Fig. 7). However, the behavior of a heavily branched polymer is similar to that of a slightly cross-linked one, and it is usually very difficult to distinguish between the two types.

The *number-average molecular weight* of a polymer affects very noticeably its mechanical properties. Impact strength, folding strength, and tensile strength are particularly adversely influenced by a low-number-average molecular weight. They assume very low values as soon as the polymerization degree of the material is around or below 100.



(a)-Crosslinked



(b)-Branched

FIG. 7.—Schematic representation of a branched and cross-linked system.

Figure 8 represents a schematic plot of tensile strength *vs.* polymerization degree of cellulose acetate and shows that the tensile strength is practically zero until a degree of polymerization of approximately 50 has been reached. Thereafter, the tensile strength rises steadily until at about a polymerization degree of 700 the curve flattens out; still greater tensile strength can be achieved only by substantially higher molecular weights. A similar behavior has been observed for most linear polymers.

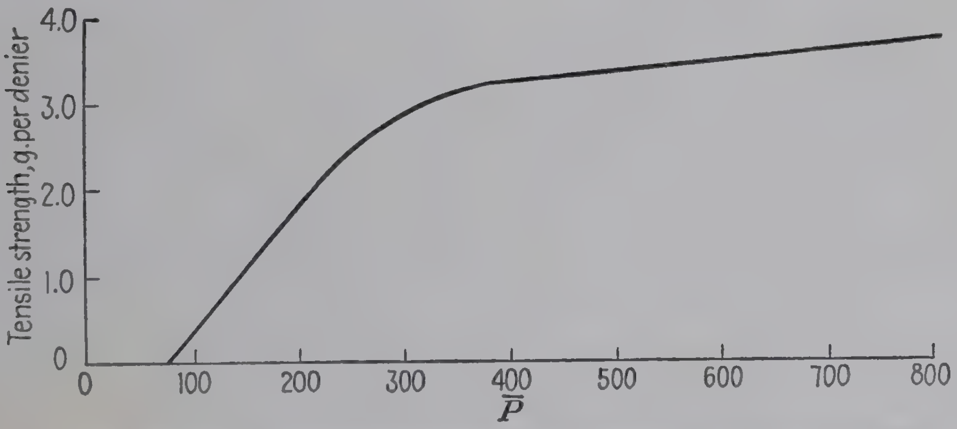


FIG. 8.—Variation of tensile strength with increasing P (cellulose acetate).

It was also found that the distribution curve of a polymeric material has a distinct influence on its mechanical properties. Curves 1 and 2 in Fig. 9 represent the distribution functions of two polymeric materials with the same average molecular weight. The product characterized by curve 1 contains a considerable portion of low-molecular-weight constituents that are detrimental to its mechanical properties. Its influence is not offset by the relatively large amount of higher molecular-weight constituents, since, according to Fig. 8, the contribution of these fractions to the tensile strength is relatively unimportant. Curve 2 shows the distribution curve of a more homogeneous polymer which has a higher impact, tensile, and folding strength because of the absence of appreciable amounts of low-molecular-weight fractions. In industrial practice, one frequently removes the lower fractions of a polymer by fractionation and improves thereby the mechanical properties of the material.

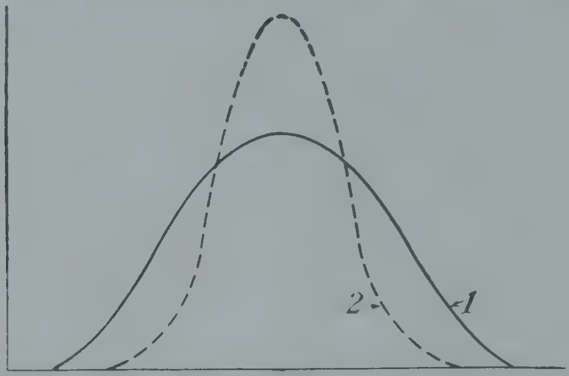


FIG. 9.—Possible distribution curves of two polymers having similar average molecular weights.

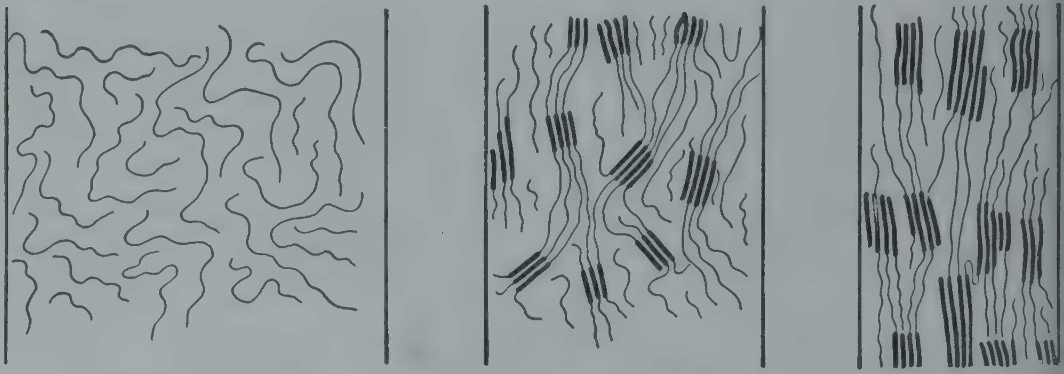

Amorphous Areas Crystalline Regions Oriented Crystallites

FIG. 10.—Arrangements of polymer molecules in respect to each other.

Another important factor that determines the mechanical properties of a polymer is the arrangement of the macromolecules in respect to one another. X-ray and electron diffraction reveals that some polymers are predominantly crystalline, *i.e.*, they possess a very high degree of geometrical order, whereas others are amorphous (low degree of geometrical order) and still others consist of coexisting regions of various degrees of order. The ordered domains or crystallites can be randomly arranged in the sample, or they can be more or less oriented in respect to a special direction, such as the axis of a fiber or the direction perpendicular to the plane of a film (Fig. 10). It seems that most samples that consist of a highly crystallized polymer with unoriented crystals can be *cold drawn* to fibers of considerable tensile strength and toughness; the most spectacular example of this behavior is Nylon. The more the original sample is drawn the better is the orientation of the crystals and the parallelization of the molecules in respect to one another, and the stronger also is the drawn fiber. If one goes too far in crystallizing a polymer and orienting the resulting crystals, a "draw" ratio results where the fibers become brittle. Figure 11 shows the highly crystalline diagram of a drawn Nylon fiber.

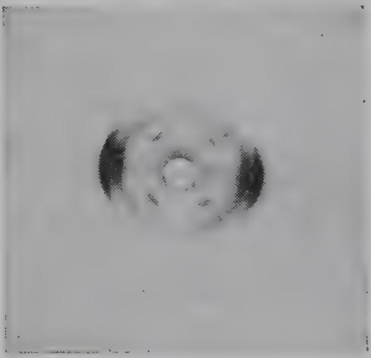


FIG. 11.—Drawn nylon.

An X-ray diffraction pattern of unstretched natural rubber is shown in Fig. 12*a*; it is typical of an amorphous polymer. Here, the individual molecules are randomly arranged, and the sample shows complete physical and mechanical isotropy. All rubbers in the relaxed state exhibit such X-ray diagrams. Upon stretching, one obtains diffraction patterns as shown in Fig. 12*b*, where obviously part of the material has crystallized while another part is still amorphous.

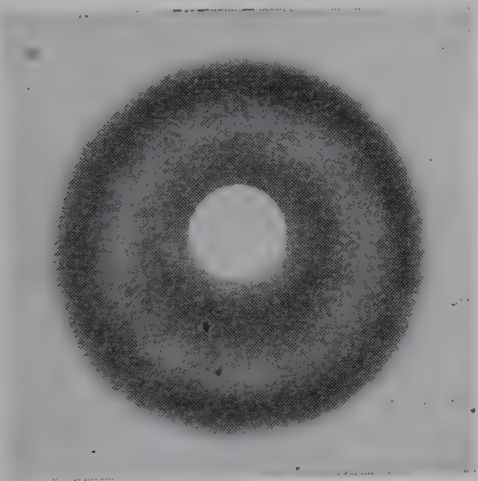


FIG. 12*a*.—Unstretched rubber.

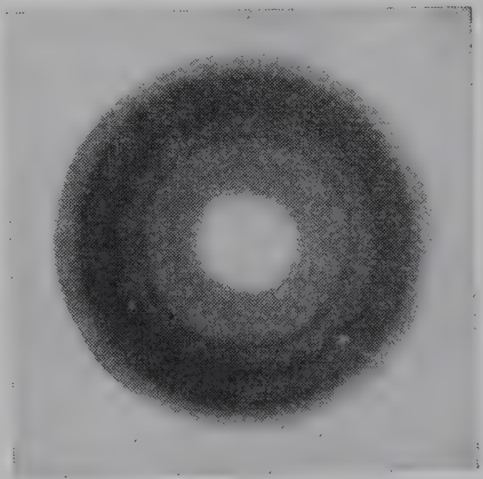


FIG. 12*b*.—Stretched rubber.

In general, typical rubbers exhibit an amorphous diagram in the relaxed state, whereas typical fibers show distinct crystallinity. In between these two extremes, a large class of materials exist that have intermediate degrees of randomness and exhibit intermediate mechanical properties. Most of these so-called plastics behave mechanically as if they were a mixture of an elastic solid and a viscous liquid; they can be molded by heat and pressure and keep their new shape after cooling down.

The three forms, then, in which high polymers may appear—*fibers*, *plastics*, and *rubbers*—seem to be dependent upon the **internal arrangement** of the long-chain molecules, which in turn is caused by the shape and flexibility of the individual molecules and by the magnitude of the forces between them. If these forces are small or the molecules are bulky and fit badly into the regular pattern of a crystal lattice, then the random distribution prevails and the material shows rubbery characteristics. Strong forces between the individual chain molecules or molecular shapes that fit easily into a three-dimensional lattice are characteristic for a polymeric material of fibrous nature. Intermediate cases, finally, lead to typical plastics. The border lines between these three types of substances are often rather indistinct; one and the same polymer may be found in different forms depending upon pressure, temperature, and changes in its molecular arrangement due to mechanical influences. Thus, natural rubber has typical fiber properties it if is slowly cooled down in the highly stretched state. A typical plastic, such as polyvinyl chloride, can be made rubberlike by plasticization, and another one, polyvinylidene chloride, can be drawn out to a fiber. Industry uses the possibility of a transition from one of the typical states into another to adjust a given polymer to special uses by establishing in it a proper balance of crystallized and amorphous domains.

V. GENERAL CLASSIFICATION OF HIGH POLYMERS

Substances denominated under the common term *high polymers* can be arranged according to various systems, depending on the particular characteristic that is to be emphasized. Most commonly they are

TABLE VI.—CLASSIFICATION OF HIGH POLYMERS

Fibers	Plastics		Elastics
	Thermoplastic	Thermosetting	
a. Polyamides *b.* Polyesters *c.* Polyurethanes *d.* Polycarbamides *e* Cellulose and cellulose derivatives *f.* Polyvinylidene chloride *g.* Polyvinyl chloride-acetate copolymers *h.* Proteins	*a.* Vinyls *b.* Cellulose derivatives *c.* Straight-chain polycondensation products	*a.* Phenols-aldehydes *b.* Urea-aldehydes, melamine-aldehydes *c.* Polybasic acids—polyalcohols *d.* Silicones *e.* Allyls *f.* Proteins-aldehydes	*a.* Butadiene and butadiene derivatives *b.* Butadiene copolymers *c.* Thiokols *d.* Isobutylene and isobutylene copolymers *e.* Polycondensation products *f.* Plasticized vinyl polymers

grouped together with reference to their mechanical behavior, their chemical structure, their mode of preparation, or their technical applications. There is always some overlapping among the various classifications and even between groups of the same system, since often one polymer rightly belongs to two or more subdivisions. For example, vinyl chloride can be classified as a plastic and also as an elastic, depending on its plasticization; Nylon can be used for molding and extruding operations but also as a fiber. Ethylene oxide polymers are made by addition polymerization, but the reaction shows some characteristics of a step process. Thus, it is difficult to devise a clear-cut classification system. For purposes of survey and demonstration, it seems adequate to arrange the industrially most important high polymers in respect to their mechanical behavior in their outstanding use. However in the following section on the preparation of high polymers by polycondensation or polymerization methods, they will be discussed according to the manner in which they are produced industrially.

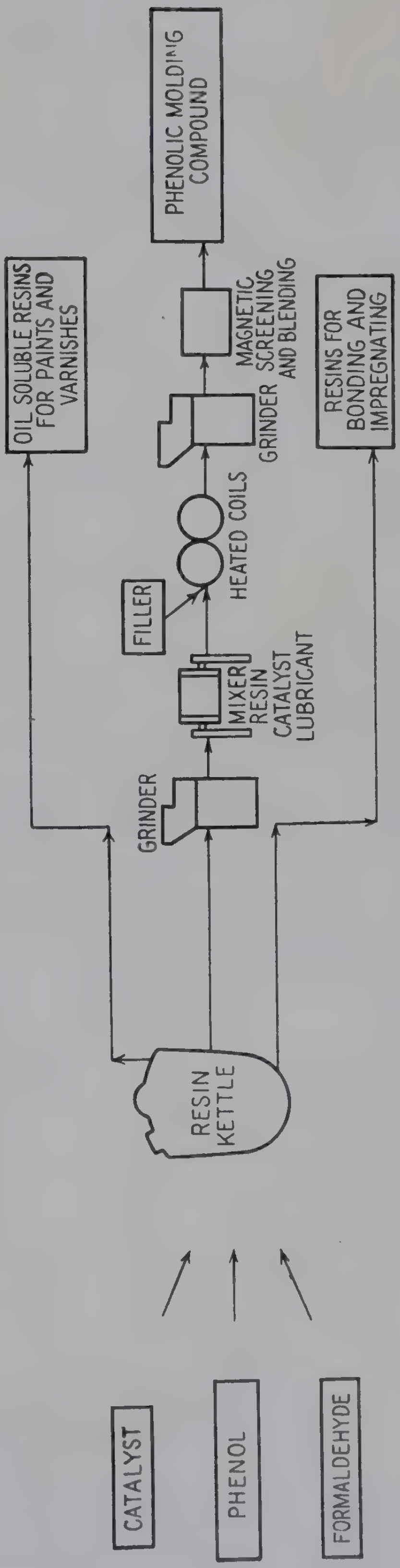

PHENOLIC MOLDING COMPOUND
OIL SOLUBLE RESINS FOR PAINTS AND VARNISHES
MAGNETIC SCREENING AND BLENDING
GRINDER
RESINS FOR BONDING AND IMPREGNATING
HEATED COILS
FILLER
MIXER
RESIN
CATALYST
LUBRICANT
GRINDER
RESIN KETTLE
CATALYST
PHENOL
FORMALDEHYDE

Fig. 13.—Flow diagram for the production of phenolic resins.

VI. THE PREPARATION AND INDUSTRIAL PRODUCTION OF POLYMERS

In principle, all the methods developed for large-scale production of high polymers are based on one of two fundamental types: (1) polycondensation and (2) addition polymerization. Although the conditions of the processes have to be adapted to the requirements of the individual monomers, the reactions of the same type are carried out basically in a similar manner, and often the same machinery can be employed for the production of various polymers. In the following, the methods of polycondensations and polymerizations will be discussed separately, and the polymers produced by them will be explained more in detail.

A. POLYCONDENSATIONS

The preparation of polycondensation products on an industrial scale roughly follows procedures employed for low-molecular condensations. The monomers are brought together in appropriate reaction vessels and mixed with the catalyst; and under the influence of heat, the polycondensation is started. In principle, two types of condensations can be distinguished: one in which the reaction is carried out in an aqueous medium and the other in which it is carried out in the melt of the monomers and polymers. The first method is used for the production of phenol-aldehyde, urea-aldehyde, and melamine-aldehyde polymers; the latter is used for the formation of polyesters and polyamides.

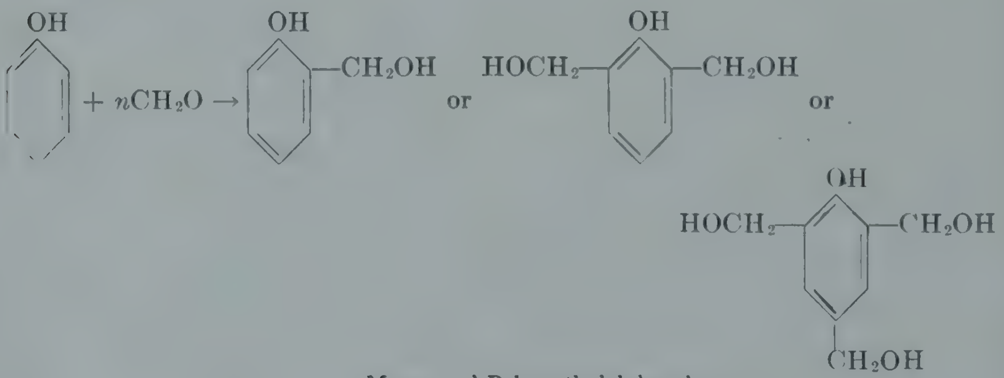
Phenol-aldehyde Polycondensations

Phenol and substituted phenols react with a number of aldehydes to give polycondensation products. Of technical importance, however, are only condensations that have either formaldehyde or furfural as the aldehyde component (Fig. 13).

Phenol-formaldehyde condensation products differ greatly in their chemical, physical, and mechanical characteristics according to

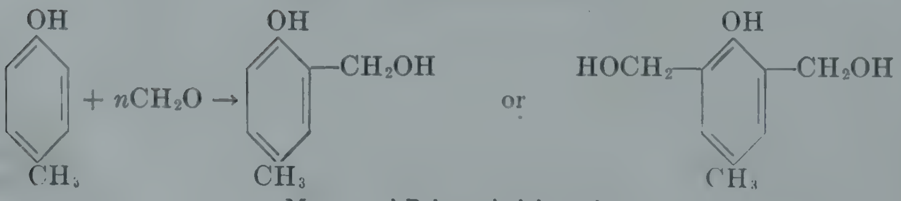
1. The proportions of phenol and formaldehyde.
2. The catalyst.
3. The type of phenol.

In all cases, the first reaction products are found to be phenol alcohols, formed by direct addition of formaldehyde to the functional positions of the phenol.



(a)

Mono- and Polymethylolphenols



(b)

Mono- and Polymethylolcresols

From there on, the course of the reaction is different and depends on the conditions chosen to obtain a specific material. Always, however, a further condensation between the phenol alcohols takes place; water and formaldehyde are split off; and the final product is composed of phenol molecules, linked together by either methylene groups ($—CH_2—$) or dimethyl ether groups ($—CH_2—O—CH_2—$).

Polycondensations, carried out in acid solution and with an excess of phenol produce soluble, thermoplastic resins called *Novolacs*. In alkaline solution, and at varying proportions of phenol to formaldehyde, the reaction proceeds in three distinct steps. During the first phase, the condensation between the phenol alcohols does not go very far, and the resin formed is soluble and fusible (*A* stage). As the reaction continues, some cross linking takes place, and in the second phase the polymers are already insoluble but still fusible (*B* stage). In the final stage (the curing process), most of the methylol groups react, and the now highly cross-linked polymer is infusible and insoluble (*C* stage) (Fig. 14).

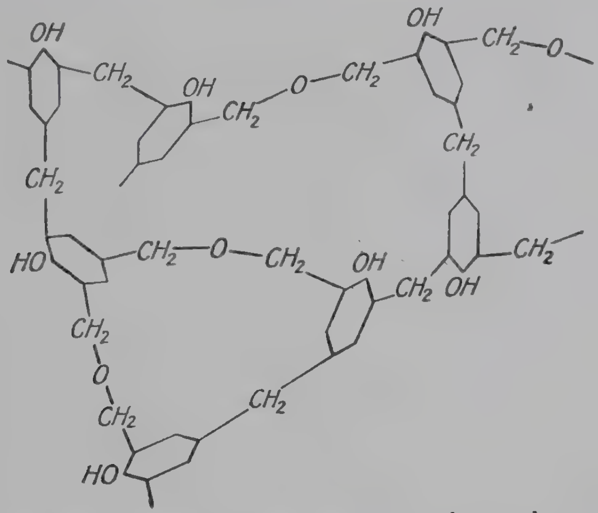
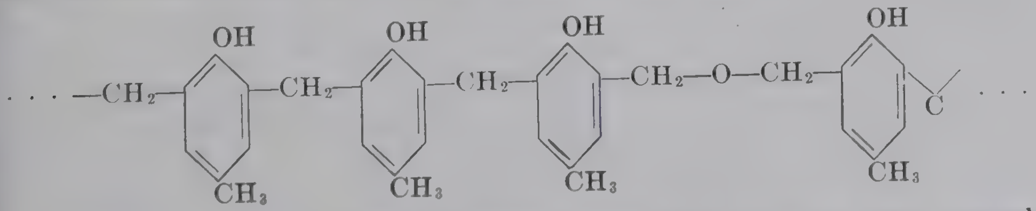


FIG. 14.—C-stage phenol-formaldehyde copolymer.

The use of ring-substituted phenols, in which the functional positions of the phenol are reduced to only two, prevents cross linking; and in both acid and alkaline mediums, linear thermoplastic resins are obtained.



Manufacturing methods for phenol-formaldehyde resins differ according to the end use to which the resin is put. If a material for *casting* purposes is desired, the reaction is carried out either at normal pressure in stainless-steel or nickel kettles at temperatures ranging from 70 to

100°C. or under CO_2 or N_2 pressure at 120 to 140°C.[1] Either acid or alkaline catalysts may be employed. The pressure treatment aids in the formation of a product free of gas bubbles, prevents discoloration of the reaction mass, and permits a shorter reaction time (Fig. 15).

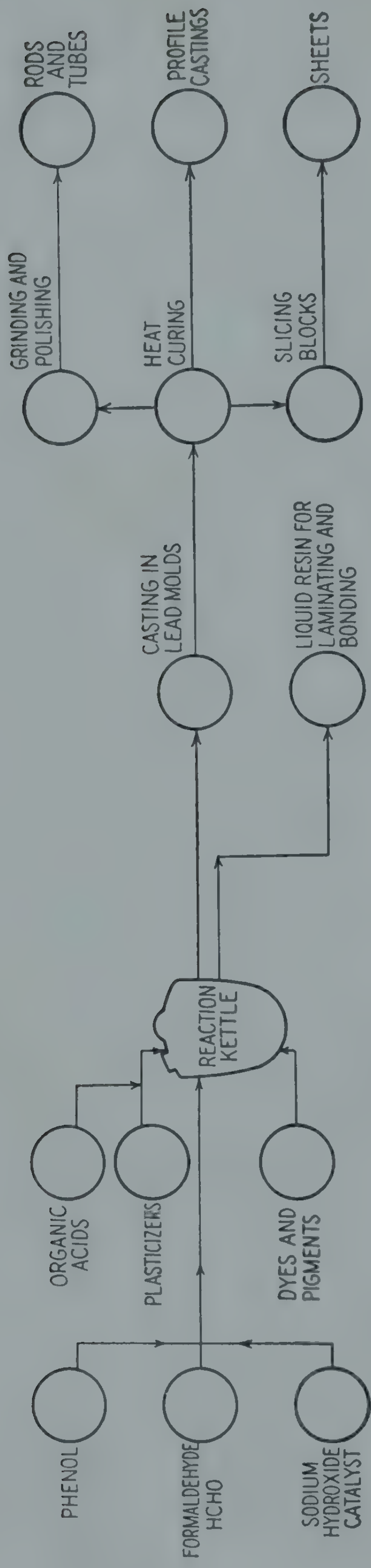

PHENOL
FORMALDEHYDE HCHO
SODIUM HYDROXIDE CATALYST
ORGANIC ACIDS
PLASTICIZERS
DYES AND PIGMENTS
REACTION KETTLE
CASTING IN LEAD MOLDS
LIQUID RESIN FOR LAMINATING AND BONDING
GRINDING AND POLISHING
HEAT CURING
SLICING BLOCKS
RODS AND TUBES
PROFILE CASTINGS
SHEETS

Fig. 15.—Flow diagram for the production of cast phenolics.

The formaldehyde-phenol ratio may vary over a range from 1 to 2.5 molecules of formaldehyde per molecule of phenol, and reaction times up to 3 hr. are necessary to convert the monomers into the desired *B* stage resin. During this time, the reaction must be closely controlled in order to achieve the correct viscosity of the mass and to assure an effective removal of the water. The mechanical and optical characteristics of the final polymer are mainly fixed during these first stages of the reaction. At the end of the reaction, the catalyst is neutralized and the light and transparent resin treated with plasticizers, dyes or pigments, and stabilizers. Glycerol is usually chosen as a stabilizer because it not only prevents fogging and clouding on aging by a control of the moisture content, but also helps to relieve stresses and strains set up during the polycondensation. The hot resin is cast into lead or glass forms and cured over a period of days at temperatures not over 80°C. Close tolerances can never be obtained, owing to shrinkage in the mold, and thus the rough casting has to be followed up by final machining operations.

The preparation of *molding powders* is carried out technically by a number of processes that are quite similar basically, but vary widely in details and refinement. The basic idea is to produce a *B*-stage resin that (1) is free of all volatile components (phenol, formaldehyde, water) and

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[1] U. S. 939,966; Ger. 233,806.

(2) can be "kicked over," *i.e.*, cured in a specified time. (Normally, the curing cycle is preferably a short one, but sometimes the specifications call for a certain predetermined time period.) Two ways exist to obtain such resins: a one-stage and a two-stage process. In the first method, phenol and formaldehyde in slight excess are reacted in the presence of acid or alkaline catalysts under continuous control of the temperature and viscosity of the reaction mix. After the resin formation has reached the desired state, the condensation is interrupted and the water removed under vacuum. The dried resin can now be mixed on hot rolls with fillers, pigments, and molding aids and, after cooling, is ground and sieved in order to ensure uniformity of particle size. Since the resin already contains the necessary amount of formaldehyde to bring about curing, all these operations must be closely watched and timed in order to prevent a premature thermosetting of the material. The main advantage of the second, the two-stage process lies in the fact that such close control is unnecessary because the amount of formaldehyde added during the first stage is insufficient for a cure. The resin otherwise is produced like a one-stage resin up to the point where fillers and other ingredients are added on heated rolls. At this second stage of the reaction, enough formaldehyde in the form of paraformaldehyde or hexamethylene tetramine is added to assure a rapid cure.

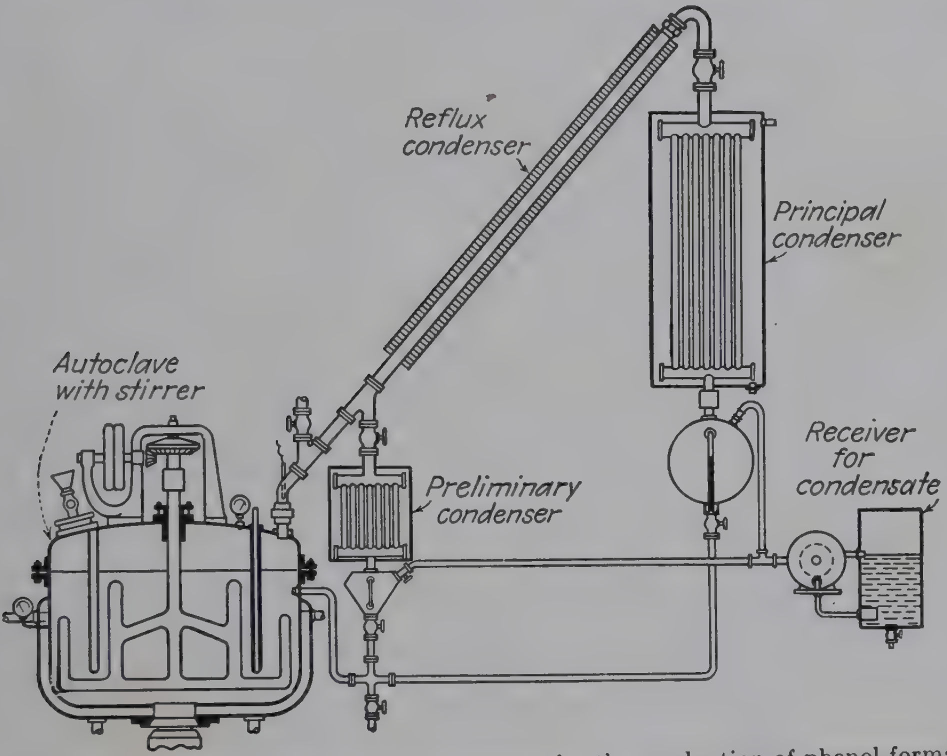

FIG. 16.—Stirring autoclave with reflux condensers for the production of phenol-formaldehyde condensation resins.

The equipment used for carrying out the polycondensation generally consists of a jacketed autoclave with stirring mechanism and reflux condenser. During the early stages of the reaction, the reflux condenser prevents losses of monomeric materials which are returned to the reactor (Fig. 16).

In the final phase of the reaction, a separation of the resinous product from the water and the unreacted part of the mix occurs. Many suggestions have been advanced and patented as to the subsequent treatment of the resinous parts. One has been mentioned before; it consists of drying the resin, incorporating fillers and other ingredients on heated rolls, and finally grinding and sieving it. There is a certain disadvantage to this method, because the unreacted phenols or low-molecular-weight condensation products are removed only with some difficulty from the reaction mix. A decrease of the stability of the product and corrosion of the equipment used might be the consequence of an incomplete removal. As an alternative, it has been suggested that the *B*-stage resins be dissolved in organic solvents[1] or, better, emulsified[2] and that the other ingredient then be added to the solution or emulsion, as the case may be. A number of additional patents describe coagulation procedures of the emulsion and drying of the final product.[3] Another possible procedure is to carry out the condensation in the presence of all the substances that are desired in the final product.[4]

Phenolic resins for *impregnating* or *laminating* purposes are prepared by procedures similar to those used for molding powders. The condensation is carried to a point where the resin possesses the desired viscosity and flow and is used as such in solutions of organic solvents or in emulsions for the impregnation of porous materials. The impregnated goods are then shaped and cured. If greater wall thickness is required, a number of layers of the impregnated material are fused together by heat and pressure in a laminating and curing process. It has also been suggested to saturate the paper or the fabric to be impregnated with the liquid monomers and to have the condensation reaction take place in the pores or on the fibers of the material.[5] In the preparation of plywood, either the wood layers may be bonded together by a viscous *B*-stage resin paste, or solutions and dispersions of the resinous paste in organic solvents or water, respectively, may be employed. Another way to obtain plywood structures is to impregnate the wood veneers with liquid, low-stage *A* resins or with a water solution of them and subsequently to cure the resins by the application of heat and pressure.

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[1] Fr. 695,699; Swiss 152,260.

[2] U. S. 1,160,362; 1,146,299; 1,146,300; Ger. 379,983; 339,426.

[3] U. S. 1,551,428; 1,703,414; 1,855,384; Brit. 384,728; Fr. 820,216; Ger. 506,129.

[4] U. S. 1,684,755; 1,692,856; Brit. 291,474; Fr. 633,540; 633,541.

[5] U. S. 1,160,362; 1,160,365; 2,083,929.

For use in the *varnish* and *lacquer* industry and for the production of printing inks, phenol and formaldehyde are condensed only to a low-stage (*A*) resin, which then is combined with either natural resins (rosin, Congo gum), synthetic resins (cumar, alkyds, ureas), or fatty acids.[1] On further reaction, the condensation process is completed, and presumably some chemical reaction between the condensate and the added products also takes place. Phenolic resins, thus modified, exhibit increased solubility in a variety of cheap solvents and are compatible with drying oils. Other types of phenolic resins, extensively used in the coating industry, are the soluble and thermoplastic condensation products of formaldehyde and alkyl phenols. They increase the adhesion of the film to the surface, are miscible with drying oil, and impart to varnishes and paints good resistance to water and aging.

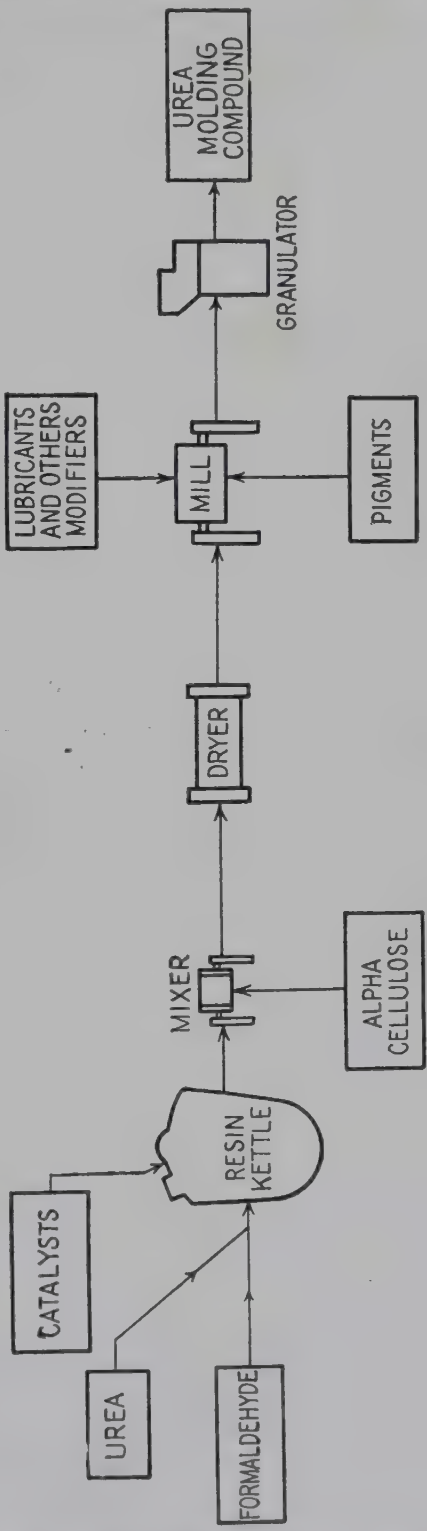
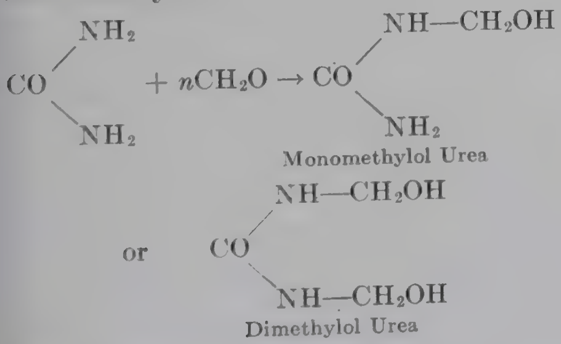

UREA MOLDING COMPOUND
GRANULATOR
LUBRICANTS AND OTHERS MODIFIERS
MILL
PIGMENTS
DRYER
MIXER
ALPHA CELLULOSE
RESIN KETTLE
CATALYSTS
UREA
FORMALDEHYDE

Fig. 17.—Flow diagram for the production of urea resins.

Urea and Melamine-formaldehyde Condensations (Fig. 17).

Mono- and dimethylol ureas can be isolated as first reaction products of a condensation between urea and formaldehyde.



$$CO(NH_2)_2 + nCH_2O \rightarrow NH_2{-}CO{-}NH{-}CH_2OH \quad \text{or} \quad HOCH_2{-}NH{-}CO{-}NH{-}CH_2OH$$

Monomethylol Urea

Dimethylol Urea

Both substances are water soluble. As the process is carried further, the methylol groups react with each other and form methylene ($—CH_2—$)

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[1] Brit. 456,723.

bridges between the remnants of the urea molecule. The completed condensation reaction leads to three-dimensional network-like molecules which impart insolubility and temperature stability to the resin (Fig. 18).

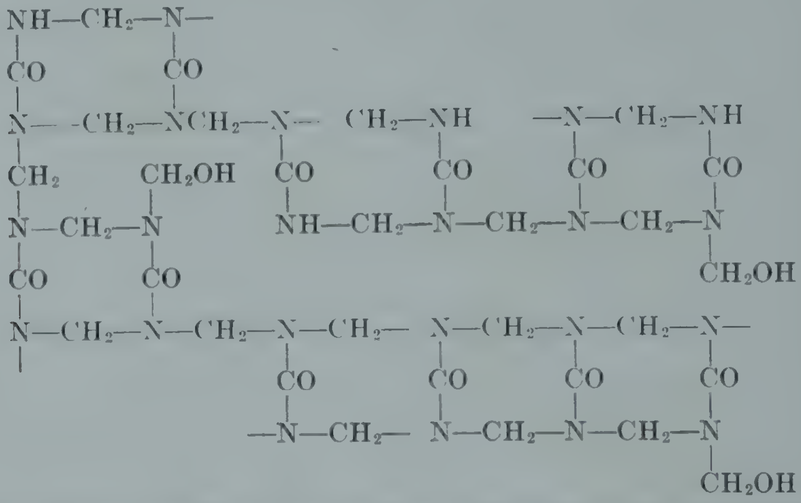
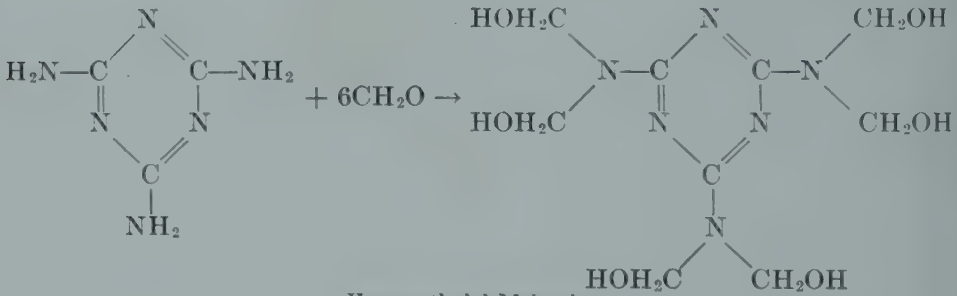


FIG. 18.—Urea-formaldehyde condensation product: structural representation.

Processes similar in principle take place in the case of melamine-formaldehyde condensations, where hexamethylol melamine can be isolated as a condensation product.



Hexamethylol Melamine

This indicates an interesting difference from the urea-formaldehyde condensation reaction. There, the addition of the formaldehyde seems to stop after a disubstituted product is formed, since only a dimethylol urea could be identified in the reaction mixture.

In technical processes, it is possible to work in aqueous solutions and to stop at a stage where the already very viscous reaction mix is still water soluble. The water is then removed under vacuum. It is also possible to proceed further to the formation of hydrophobic, higher condensed resins, which can be mechanically separated from the aqueous medium and dried separately. Other methods are to carry out the initial condensations with a minimum of water present,[1] or one can work in organic

[1] U. S. 2,101,534; Brit. 442,603; 483,399.

solvents.[1] "Dry" processes also are known, in which paraformaldehyde or hexamethylene tetramine are used as suppliers of formaldehyde.[2]

The temperature of the reaction may range from room temperature to the boiling point of the medium, and the ratio of urea or melamine to formaldehyde may vary from 1:1 to 1:3 moles of formaldehyde to urea. The temperature of the reaction and the proportion of the components must be correlated with the pH of the reaction mix, which is of outstanding importance for the course of the reaction. It can be generally said that in an alkaline medium the reaction proceeds more slowly and can be stopped easily at a stage in which the condensation products are still water soluble (*A* stage). After drying, these products can be converted into insoluble products by heat and acid catalysts or by acid catalysts alone. If the condensation is started with an acid condensation catalyst, then it quickly results in the formation of water-insoluble resins (*B* stage) that must be stabilized by buffer agents in order to prevent setting during the necessary drying process. For the conversion into the final and cured resin, acid catalysts are again added to overcome the action of the buffering agents.

On an industrial scale, the polycondensation is carried out in equipment similar to that used in phenol-formaldehyde condensations. The corrosion resistance of the parts that are in contact with the reaction mix must be emphasized more than in the production of phenolics because of the strong alkalinity or acidity of the reacting solution. The condensation is carried to a stage that is most favorable as a basis for the subsequent operations of casting or compounding to molding powders. For most purposes, this stage is reached when the solution of the low-molecular-condensation products has become very viscous and when, by further removal of water under vacuum, a resin paste is obtained. For casting purposes, the paste is then specially treated by dehydration operations and the further addition of urea or thiourea. Cast resins from urea or melamine, however, are of only minor industrial importance because it has not yet been possible to convert the resin, which is at first crystal clear and uniform, into a material that does not develop tiny cracks and crevices on aging.

In the production of molding powders, this disadvantage is largely overcome by incorporating into the condensate fillers that take up the internal strains and stresses of the cured resin. Cellulose has been found to be a very satisfactory filler because it does not greatly impair the transparency of the clear mold. Other fillers, such as wood flour, paper, and cotton linters, are used for opaque or colored molding powders. The incorporation of these, together with dyes, pigments, lubricants, and accelerators, is carried out while the resin is still wet. The thoroughly mixed paste is finally dried to a moisture content of 3 to 5 per cent and ground.[1]

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[1] U. S. 1,699,245; Brit. 359,147; Fr. 688,185; Ger. 535,438.

[2] U. S. 1,863,426; Brit. 262,148; Ger. 512,566.

The manufacture of resins for use as adhesives or laminating agents, for textile-finishing operations, or for the impregnation of fabrics, paper, and wood is similar to that of cast resins. Also, special alcohol-soluble resins, which are employed in the varnish and lacquer fields, can be made by completing the condensation of low-stage resins in the presence of aliphatic alcohols. Some of the available methylol groups of the resin react with the alcohols by ester interchange and impart to the finished condensate an increased solubility in, and compatibility with, other film-forming products.

Condensations Leading to Polyesters

Condensation reactions between dihydric alcohols and dibasic organic acids, or condensations of oxyacids, result in the formation of linear and thermoplastic polymers of no significant industrial importance. However, the condensation products of polyhydric alcohols and acids, the so-called alkyds and modified alkyds, are widely used in the paint and varnish industry (Fig. 19).

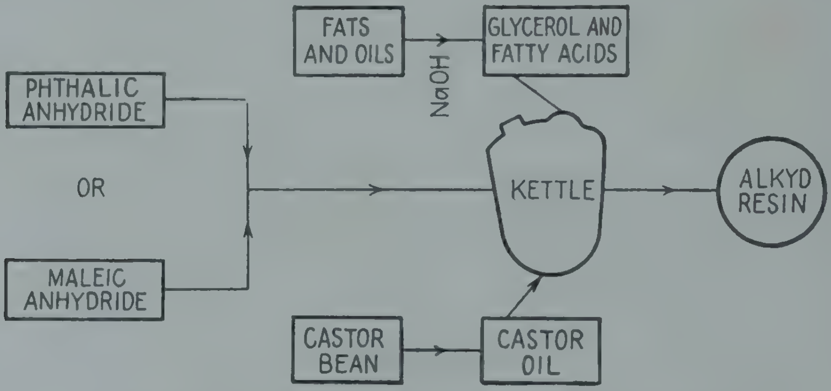

FIG. 19.—Flow diagram for the production of alkyd resins.

The most valuable of these resins are made by reacting glycerol or pentaerythritol with phthalic anhydride, maleic anhydride, and with adduct compounds of maleic anhydride, obtained from a diene synthesis of the latter with substances having conjugated double-bond systems.

Figure 20 is a schematic presentation of a heavily cross-linked tridimensional molecule such as could be expected from the reaction of a trifunctional alcohol and a bifunctional acid. The technical process is carried out by heating the alcohols and acids together and removing the water formed during the reaction by efficient stirring and the application of a vacuum. The addition of acidic or alkaline catalysts is recommended, though the polycarboxyllic acids themselves act as catalysts.

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[1] U. S. 1,904,243.

Figure 21 shows a schematic layout of equipment employed for such polycondensation procedures, in which unmodified and modified alkyd resins can be produced. Unmodified alkyds have a tendency to become insoluble and infusible on prolonged heating and moreover are of only limited compatibility with many film-forming materials. To overcome these disadvantages, monobasic long-chain organic acids are built into the polymer molecule; they esterify one of the functional OH groups of the glycerol and leave only two more functional groups on the alcohol. A polycondensation with phthalic anhydride thus yields a permanently soluble and fusible resin, to which the long hydrocarbon chain of the added monobasic acid imparts (1) better solubility in cheap lacquer

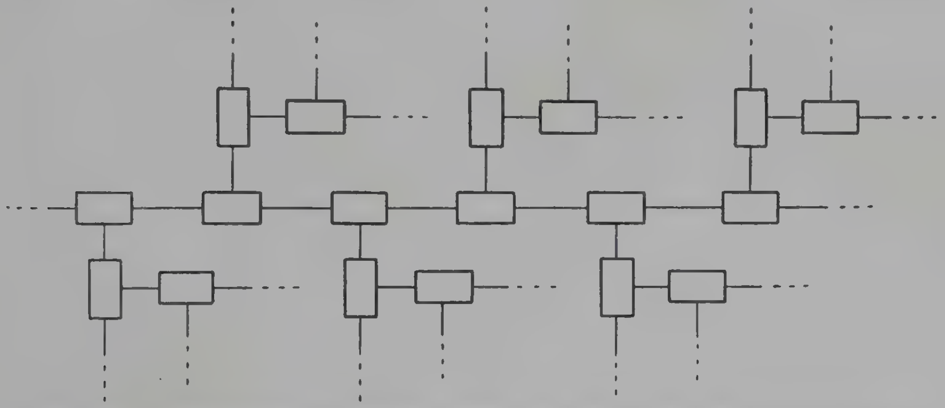

FIG. 20.—Tridimensional polymer from dibasic acid and polyhydric alcohol.

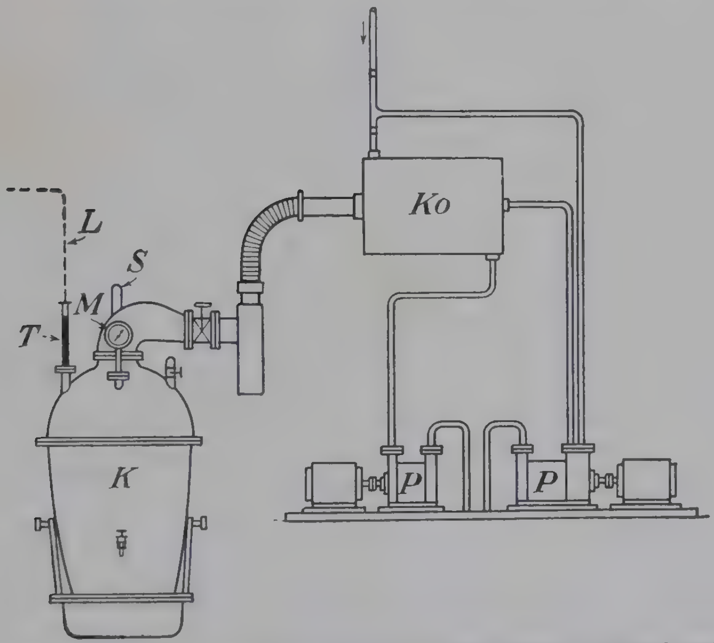

FIG. 21.—Schematic layout: equipment for the preparation of alkyd resins. *K*, Reaction kettle; *Ko*, condenser; *T*, *L*, recording thermometer; *M*, manometer; *P*, liquid and vapor pumps.

and varnish solvents and (2) compatibility with drying and semidrying oils.

Condensations Leading to Polyamides

Among the most important high polymers developed during the last decade belong the products obtained from a polycondensation of diamines and dibasic acids (*a*) or resulting from an amino-acid polycondensation (*b*).

$$\begin{array}{l} n\,NH_2{-}(CH_2)_x{-}NH_2 + n\,HOOC{-}(CH_2)_y{-}COOH \\ \qquad\downarrow \\ NH_2{-}(CH_2)_x{-}NH{-}[{-}OC{-}(CH_2)_y{-}CO{-}NH{-}(CH_2)_x{-}NH{-}]_{n-1} \\ \qquad\qquad {-}OC{-}(CH_2)_y{-}COOH + {}_{2n-1}\,H_2O \end{array} \tag{a}$$

$$\begin{array}{l} n\,NH_2{-}(CH_2)_x{-}COOH \\ \qquad\downarrow \\ NH_2{-}(CH_2)_x{-}CO{-}[{-}NH{-}(CH_2)_x{-}CO{-}]_{n-2}{-}NH{-}(CH_2)_x{-}COOH + {}_{n-1}H_2O \end{array} \tag{b}$$

These polyamides are substances of high-softening temperatures (approximately 150 to 300°C.), insoluble in most organic solvents and easily extruded to fibers of high tensile strength. The most widely produced polyamide type is Nylon, which is made from hexamethylene diamine and adipic acid. For a good working procedure it is suggested that the salt of the diamine and the diacid be precipitated first from a dilute alcohol solution of both ingredients.

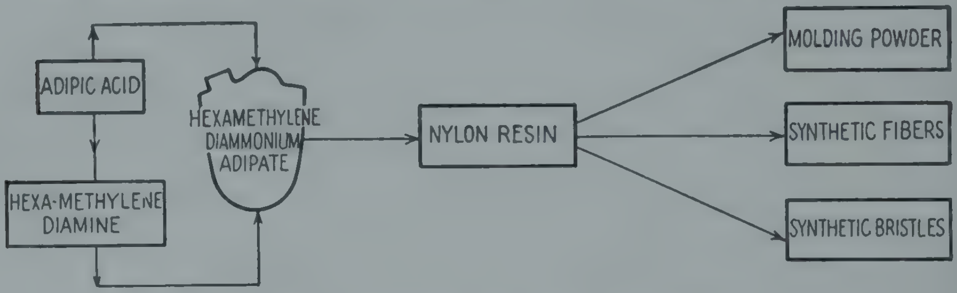

FIG. 22.—Flow sheet for Nylon production.

$$\begin{array}{c} NH_2{-}(CH_2)_6{-}NH_2 + HOOC{-}(CH_2)_4{-}COOH \\ \downarrow \\ NH_2{-}(CH_2)_6{-}NH_3{-}OOC{-}(CH_2)_4{-}COOH \end{array}$$

The salt is purified by recrystallization and is subsequently heated, in a nitrogen atmosphere, in glass-lined or stainless-steel autoclaves.[1] The temperature is kept at 280°C., and overheating is prevented by the addition of small amounts of phenols or water.[2] The progress of the reaction can be controlled by viscosity measurement of the melt, by electrical-resistivity measurement, or empirically by the ease with which the condensate can be drawn out to fibers. In the last stages of the process, the water obtained as a reaction by-product must be removed by the application of a vacuum (Fig. 22).

In order to increase the solubility in organic solvents and moreover to keep the average molecular weight from getting above the range of 10,000 to 20,000 (in which case the softening range would become too high), monofunctional amines or organic acids may be added in small amounts.[1] After the reaction is finished, the melt is filtered and pressed through the fine openings of spinerets,[2] whereby a certain amount of stretching of the fiber occurs. Subsequent stretching greatly increases the tensile strength of the filament, so that it exceeds even silk in this respect. The melt can also be poured on a rotating drum and flaked after cooling. The flakes are used for molding purposes or for the preparation of sheets and foils.

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[1] U. S. 2,163,584; 2,165,253.

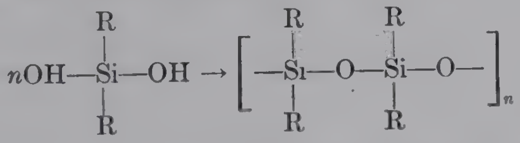
[2] U. S. 2,163,636; Brit. 506,125; Fr. 842,325.

Following the same principles and methods of a polyamide production from hexamethylene diamine and adipic acid, a whole series of polycondensation products can be prepared by variation of the chain length of both the diacids and the diamines and by substitution. Even thermosetting types can be produced by condensation of adipic acid and diethylene triamine. The diversity of properties exhibited by these polymers and the possibility of controlled changes of their characteristics promise their widespread application in many fields of industry.

Silicones

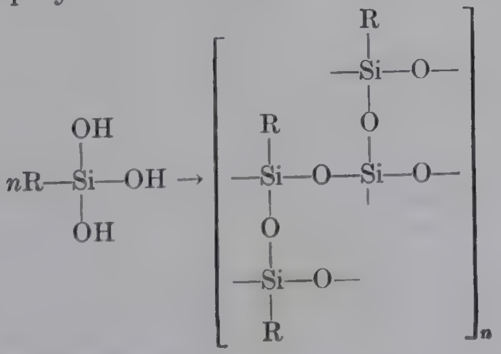
Recently a group of high-polymeric substances has been developed that are structurally based on a framework of Si—O and Si—C bonds. Two or more functional groups can be attached to the tetravalent silicon atom, and polycondensation reactions between such bi- or poly-functional silicon derivatives may lead to chain or cross-linked polymers. The following schematic formulas in which the functional groups are represented by hydroxy groups elucidate this further.

Polycondensations between silandiols yield straight-chain polymers,



$$n\mathrm{OH{-}}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}\mathrm{{-}OH} \rightarrow \left[\mathrm{{-}}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}\mathrm{{-}O{-}}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}\mathrm{{-}O{-}} \right]_n$$

whereas similar reactions between silantriols result in the formation of highly cross-linked polymer molecules.



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[1] U. S. 2,149,286; Brit. 495,790.

[2] U. S. 2,071,251.

In many respects these processes follow the familiar pattern encountered in carbon chemistry but they differ decidedly from it in two major aspects. First, the strength of the Si—O bond greatly exceeds the strength of the Si—Si or the Si—C linkages. Consequently, there is a strong tendency for the two elements to combine and to build up polymers in which this link constitutes the structural unit. It has been found, on the other hand, that chain molecules are unstable and hydrolize easily if the number of consecutive Si—Si bonds exceeds five. This is in contrast to the carbon high polymers where the C—C bond is the essential unit of the molecule.

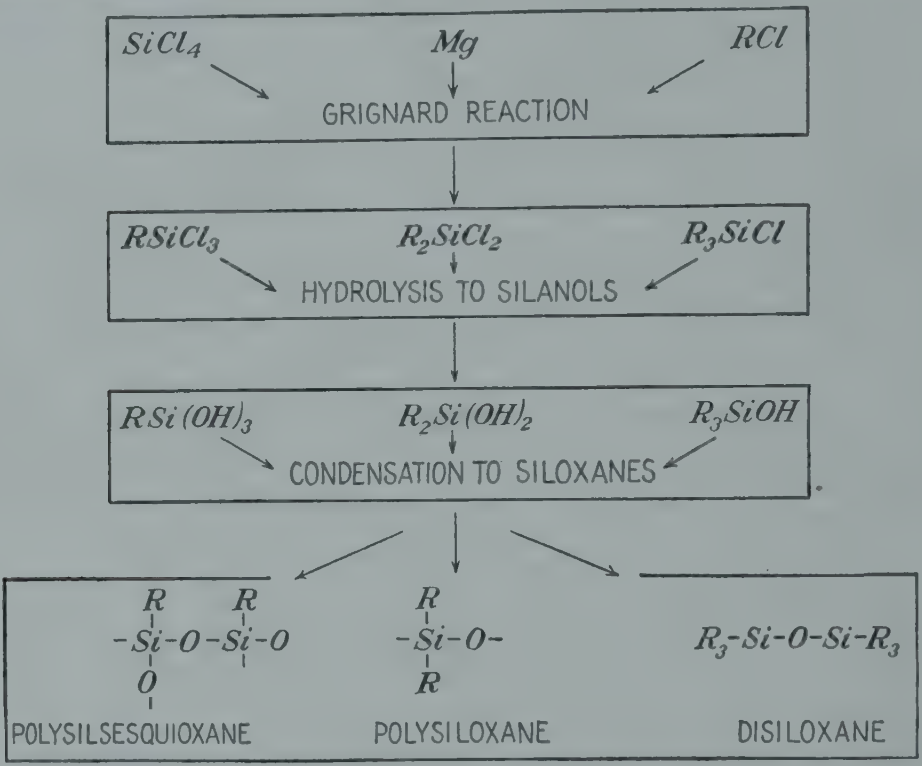

SiCl4
Mg
RCl
GRIGNARD REACTION
RSiCl3
R2SiCl2
R3SiCl
HYDROLYSIS TO SILANOLS
RSi(OH)3
R2Si(OH)2
R3SiOH
CONDENSATION TO SILOXANES
R R
-Si-O-Si-O
O
R
-Si-O-
R
R3-Si-O-Si-R3
POLYSILSESQUIOXANE
POLYSILOXANE
DISILOXANE

Fig. 23.—The formation of silicones.

The second important difference lies in the fact that reactions of carbon compounds tend to produce only five- or six-membered rings in any appreciable amount whereas silicon rings of relatively large size may be formed quite readily. It seems, therefore, that cyclization competes more seriously with chain-polymer formation in the reactions of the silicon atom than it does in carbon chemistry.

The polymers that so far have proved most interesting from a technical point of view are those prepared by polycondensations of silanols, the hydroxy derivatives of organo-silicon compounds. They, in turn, are usually made by a hydrolysis of silane halides, though it is known that sulfuric esters of silicones also can be readily hydrolyzed. The synthesis of silane halides, which are organo-silicon derivatives with one, two or three halogens as substituents on the silicon atom

$$R_3SiX,\ R_2SiX_2,\ RSiX_3,\ RSiHCl_2$$

can be conveniently carried out with the aid of the Grignard reaction, by reacting silicon tetrachloride with alkyl magnesium salts (See Fig. 23).

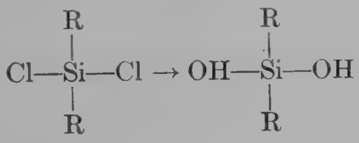
$$SiCl_4 + RMgBr \rightarrow RSiCl_3 + MgBrCl$$
$$RSiCl_3 + RMgBr \rightarrow R_2SiCl_2 + MgBrCl$$

A more direct way of preparing silane halides, involving the reaction of silicon with alkyl or arylhalides, with or without the use of copper or silver catalysts, has been proposed.

$$Si + 2RCl \rightarrow R_2SiCl_2$$

Both methods, however, produce a mixture of the various silane halides, which often are difficult to separate. Since the presence of even small amounts of trifunctional molecules may produce sufficient cross linking to render the polymers insoluble or to cause unwanted gelation, the problem of thorough purification is an important one if liquid or thermoplastic silicones are desired.

The hydrolysis of the silane halides to silanols

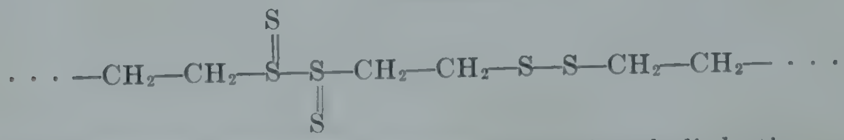


$$Cl-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-Cl \rightarrow OH-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-OH$$

and the condensation of the latter are generally performed in one step. As previously mentioned, cyclization takes place simultaneously with the formation of chain or cross-linked polymers; and in some of the commercially available materials, 50 per cent of the molecules have ring structures.

"Silicones" has become a generic name given to a variety of products manufactured on an industrial scale by condensation processes of organo-silicon compounds. They comprise oily liquids of different degrees of viscosity, light and heavy greases, substances exhibiting rubberlike characteristics, and thermoplastic and thermosetting resins. Many of the silicones have rather unusual properties, which make them suitable for special applications. For instance, the oils show a low rate of change in viscosity over a wide range of temperature and can therefore be used as lubricants in arctic and tropical climates. Films of certain silicone oils adhere so tenaciously to paper, fabric, glass, and metals that they render the surfaces water repellent to a very high degree. The silicone rubbers show better heat and aging resistance and are flexible at lower temperature but have less tensile and tear strength than other synthetic and natural rubbers. The resinous silicones are particularly useful in applications where high heat resistance, inertness to chemicals and solvents, and good electrical characteristics are needed. Coatings have been prepared from these resinous silicones that have proved to withstand temperatures up to 260°C. for considerable time periods. They are used as insulating varnishes for electrical devices.

Thiokols



$$\cdots\text{—CH}_2\text{—CH}_2\text{—}\overset{\overset{\textstyle S}{\|}}{S}\text{—}\underset{\underset{\textstyle S}{\|}}{S}\text{—CH}_2\text{—CH}_2\text{—S—S—CH}_2\text{—CH}_2\text{—}\cdots$$

Polycondensation processes between bifunctional aliphatic compounds and polysulfides of the alkali and alkali earth metals lead to polymers of varying consistency. The basic reaction

$$n\,\text{XCH}_2\text{—R—CH}_2\text{X} + n\,\text{Na}_2\text{S}_4 \rightarrow \text{—(CH}_2\text{—R—CH}_2\text{—S}_4)n\text{—} + 2n\,\text{NaX}$$

indicates that the alkyl groups are linked by sulfur molecules, the valency of which is determined by the particular polysulfide used in the reaction. The most interesting in this group of condensation polymers are those which exhibit rubberlike properties and are manufactured under the name of polysulfide rubbers (Thiokols).

The reactants for the type of rubber mainly produced in the United States are ethylene dichloride and sodium tetrasulfide. The elasticity of the polymer may be changed by variation of the amount and the nature of the dihalogenide, and its solubility seems to depend on the sulfur content of the polysulfide.[1]

The condensation reaction may be carried out in an aqueous solution of the components under application of heat and in the presence of an alcohol or a ketone. Preferably, however, emulsifying or dispersing agents are added to the aqueous medium, and the polymer is obtained in the form of a more or less stable suspension, depending on the effectiveness of the added dispersing agent.

Simultaneously with the formation of long-chain polycondensation products, some low-molecular cyclic compounds that cause an unpleasant odor are produced in the reaction. To remove such substances and decrease the amount of sulfur present in the polymer chain, the material is treated with any of a number of chemicals that may serve as reactants or solvents for the sulfur and the cyclic compounds. The fact that two sulfur atoms may easily be removed from the chain seems to sustain the validity of the structural formula of the chain polymer as given above. Some of the links between the alkyl groups consist of tetravalent sulfur atoms, while other sulfur atoms revert to their bivalent state.

The mechanical properties of the polysulfides may be enhanced by curing processes. The polymers can be compounded in such a way that their elasticity and resilience approximate that of natural rubber. The outstanding characteristic of the materials is their inertness to organic solvents, petroleum hydrocarbons, and lubricating oils. A drawback of the polysulfide rubbers, *viz.*, a certain amount of plastic flow, has recently been overcome by using monomers that have residual functional groups left after the polycondensation reaction and thus provide points of attack for cross linking between the chains.

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[1] U. S. 1,890,191; 1,996,486; Brit. 302,399.

B. POLYMERIZATIONS

The Methods of Polymerization

The simplest way to carry out an addition polymerization reaction of a vinyl type monomer ($CH_2{=}CHX$) is to let it stand at room temperature over prolonged periods of time. However, not only is this procedure economically unfavorable if attempted on an industrial scale, but the reaction itself is exothermic and may get out of hand if spontaneous polymerization starts in large masses. Technical polymerizations are, therefore, always carried out under controlled heat and catalyst conditions which are closely followed throughout the course of the reaction. Depending on economic considerations and on the use to which the polymer is put, one of four possible methods of polymerization can be employed:

1. Polymerization in bulk (mass or block polymerization).
2. Polymerization in solution.
3. Polymerization in emulsion.
4. Polymerization in suspension.

Each of them has its advantages and disadvantages, but the progress in polymerization technic during recent years and the better understanding of the principles of the reactions have enabled industry to employ all four methods for large-scale production of polymers.

Bulk (Mass) Polymerization.—This type of polymerization reaction is accomplished by subjecting the *pure* liquid or gaseous monomer to polymerizing conditions. The main problem in this procedure is the efficient dissipation of the heat of the reaction (in most cases between 10,000 and 20,000 cal. per mole), a matter that becomes increasingly difficult to achieve as the polymerization proceeds, and the increased viscosity of the reaction mass renders agitation more and more difficult. On the other hand, the advantage of bulk polymerization lies in the fact that, with proper precautions, optically clear polymers free of air bubbles and impurities and without the tiny cracks and crevices that often impart a haze to otherwise clear materials can be obtained.

Many suggestions have been made in regard to the details of the polymerization procedure. If small objects of intricate designs are desired, the monomer can be polymerized in glass forms at moderate temperature.[1] The mold shrinkage is precalculated, and the size of the forms adapted to it. This process fails if the objective of the polymerization is larger blocks or sheets. In that case, polymerization can be carried out in large forms at moderate temperatures at first, until a certain amount of conversion has taken place, whereupon the reaction is finished at higher temperatures.[2] Another process involves a stepwise polymerization in which small amounts of monomer are almost completely converted first and then new monomer is added as the reaction proceeds.[3] Addition of retarding agents, plasticizers, or mixtures of monomers of varying reactivity offers another means of controlling the reaction.[4] The prevention of the formation of air bubbles or of internal strains and stresses in the polymer can be achieved by the application of pressure,[5] by intermittent heating and cooling of the polymerizing mass,[6] or by use of molds having mobile walls.[7] If no special emphasis is placed upon utmost clarity of the product, the polymerization process can be performed in roomy kneading machines where a granulated polymer is produced, eliminating the necessity of a further grinding operation.[8]

For economic reasons, it is often advantageous to employ continuous processes instead of polymerization in batches. This has been accomplished for the polymerization of styrene by the use of towers into which prepolymerized monomer-polymer mixtures are fed at the top at temperatures of 120°C. and continue polymerization during their downward passage through the tower, leaving it at the bottom at a temperature of 180°C.[9] A further continuous method consists in spraying prepolymerized monomer-polymer mixes into a room filled with inert gases at high temperature. The final polymerization is completed in a few seconds, and the polymer appears in granular form.[10] An interesting procedure for the preparation of tubes consists in the polymerization of a monomer in tubular forms that rotate horizontally at a high speed along their longitudinal axis.[11] If mild polymerization conditions are chosen, tubes produced in this manner exceed in quality those made by extruding or molding processes.

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[1] Ger. 261,687; 261,688; 290,544; 291,299.

[2] U. S. 2,044,579; Brit. 460,251; Ger. 675,032.

[3] U. S. 1,710,825; Brit. 261,406; Ger. 446,562.

[4] U. S. 2,181,739; Brit. 419,357; 459,056; 472,242.

[5] U. S. 2,136,422; 2,136,423; 2,136,424.

[6] U. S. 2,008,719.

[7] U. S. 2,045,660; Brit. 417,999; 469,564; 471,882.

[8] Brit. 471,755; Fr. 750,348; 803,009.

[9] Brit. 381,693; 383,002; 383,216; 723,440; 834,064; 843,845.

[10] Ger. 693,889.

[11] U. S. 2,057,673; 2,057,674; Brit. 475,552; Fr. 820,450; 821,383.

As previously mentioned, bulk polymerization has proved valuable for obtaining products suited for optical purposes or for casting small objects of intricate design and in small quantities, where molding operations would be too costly. It has not, however, been widely employed for large-scale production of molding powders, lacquer resins, or other applications where huge quantities of polymers are desired. In addition to the difficulty of heat control of the reaction, the product has a rather low average molecular weight and a relatively wide spread of the molecular-weight distribution curve. These characteristics, detrimental to the mechanical properties of the mass-polymerized material, are definite disadvantages of this method and are a result of local overheatings of the polymerizing mass. Significant temperature gradients can hardly be prevented in large batch operations.

Solution Polymerization.—The disadvantage of a continuous and elaborate heat control, which is necessary in bulk polymerization, is completely overcome if the monomers are dissolved in suitable solvents and the polymerizations carried out in solution. The heat created during the reaction is now dissipated over the whole solvent-solute system, and the upper temperature limit is governed by the boiling point of the solvent medium. This eliminates overheating and ensures a smooth course of the reaction. The limited temperature range, however, allows only a certain speed of reaction. The reaction is also slowed down by the solvation of the monomer molecules, which considerably decreases the number of possible collisions of monomers per unit of time. Thus the nature of the solvent and the concentration of the monomer are the determining factors for the progress of the polymerization at a certain temperature, which progress, however, never reaches the speed of a bulk polymerization.

The resulting polymers are of relatively low average molecular weight and cannot be completely freed of traces of the solvent. Again, the nature of the solvent may influence the molecular weight of the polymerization product, since solvents may act as chain breakers or chain-transfer agents for specific monomers. For instance, it is possible to obtain products of relatively high average molecular weight by polymerizing styrene in toluene. When, however, carbon tetrachloride is used as a solvent for styrene, then the polymerization yields considerably lower average-molecular-weight material.

In comparison with other methods, the solution polymerization is therefore at a certain disadvantage, yielding in a slow reaction a low-average-molecular-weight product that cannot be obtained free of traces of the solvent. This limits its use for industrial operations, and the quantity of polymers produced in this way is indeed small. The procedure itself is simple and consists of heating the solution of monomer and catalyst until the desired degree of conversion is reached. The remaining monomer and the solvent can be removed by either steam distillation or the application of vacuum.[1] The polymer can also be separated from the solvent by the addition of liquids acting as a precipitant for the polymer.[2] A continuous process can be achieved by passing the monomer solution under pressure through heated tubes.[3]

A slight modification of the solution-polymerization method is of greater industrial importance. According to various suggestions, the monomer is mixed with a liquid that, while being a solvent for the monomer, precipitates the polymer from the solution.[4] The polymer can be removed from the reaction mixture; and with the addition of new monomer, the process can be made continuous (see page 863).

Emulsion Polymerization.—The disadvantages encountered in the two previously discussed methods, *viz.*, difficult heat control in bulk polymerization; low-molecular-weight products, slow reaction, and presence of traces of solvents in solution polymerization, are all successfully overcome by polymerization of one or more monomers in an emulsified phase. The liquid or liquefied monomers are brought into the emulsified state by any of the customary commercial means and appear in the emulsion as spherical particles of sizes ranging between 1 and 10μ (Fig. 24). During polymerization under the influence of heat and appropriate catalysts, the average particle size decreases to about one-tenth of its starting size, and the polymer is usually obtained in the form of a very stable emulsion called a *latex*. The temperature of the process is easily controlled, since the heat of the reaction is immediately taken up by the aqueous medium; any overheating is thus effectively prevented. The reaction proceeds very rapidy as compared with bulk and solution polymerizations, and the average molecular weight of the resulting polymer is considerably higher than that of a product obtained under similar conditions by either one of the two other methods. For these reasons, the emulsion-polymerization method has become of outstanding industrial importance, and a major part of large-scale processes are now carried out in this manner.

In spite of its widespread technical use, the fundamental principles and the mechanism of this type of polymerization are still not completely understood. This is partly due to the complexity of the heterogeneous system of an emulsion itself, which only in recent years has been sufficiently cleared up to allow an investigation of polymerizations taking place in such systems. Although a considerable number of patents pertain to empirical rules and conditions of emulsion polymerization and date back as far as 1912[1], it was only around 1936 that an explanation of the mechanissm of the reaction was attempted. Further research since then has indicated that the polymerization does not start or proceed to an appreciable extent inside the emulsified particle itself. It seems, rather, to take place in that part of the monomer which is solubilized in the aqueous phase and also on the interface of the particle and the emulsion medium. Extensive investigations are now being undertaken in order to determine the exact location of the initiation, propagation, and termination steps of the polymerization and to clarify their kinetic conditions.

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[1] U. S. 1,855,413; Brit. 319,590; Fr. 663,711.

[2] Brit. 406,338; Fr. 843,622.

[3] Brit. 319,588.

[4] U. S. 2,121,839; Brit. 336,897; 404,504; 437,284; 453,578; Can. 353,925; 362,232; Fr. 753,045; 789,857.

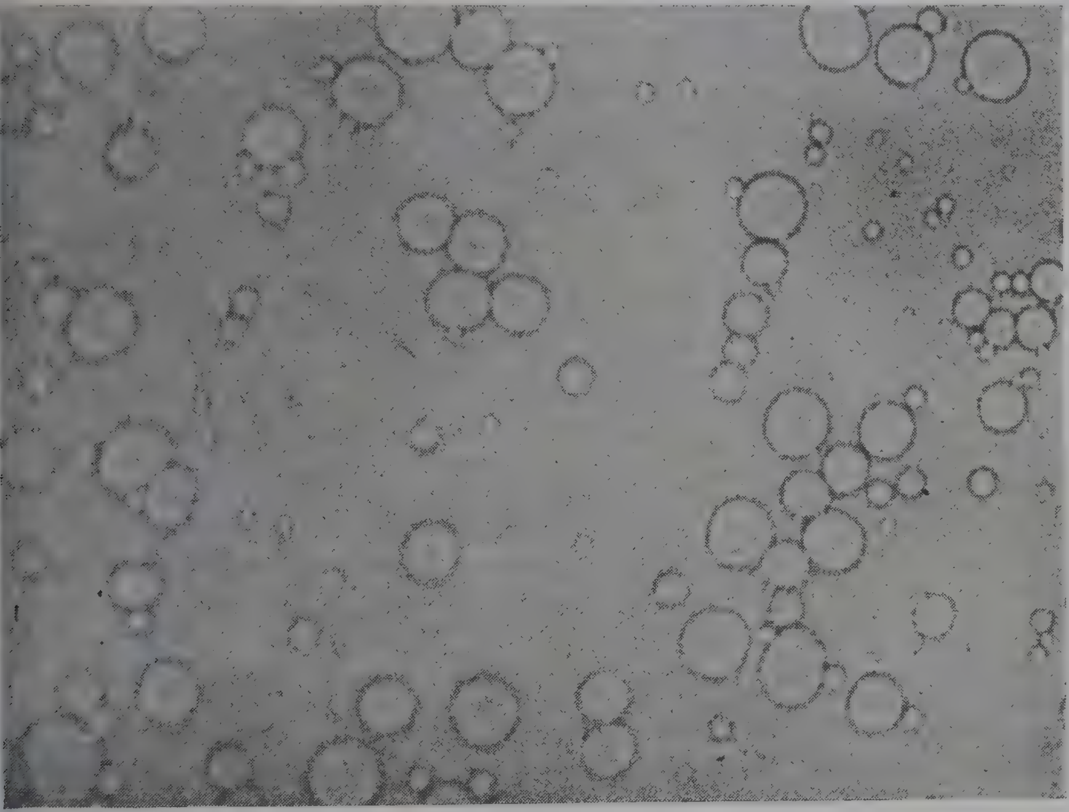

Fig. 24.—Monomer particles obtained by emulsion polymerization.

In industry, the process is mostly carried out in kettles that have adequate means of agitation and are equipped with reflux condensers. If one of the monomers is a gas or a low-boiling liquid, the polymerization is performed in a closed system capable of sustaining the pressure developed as a consequence of the increased temperature. Agitation here is provided by pressure-tight stirring devices or by the rocking or tumbling of autoclaves. One way to control the temperature is by intermittent heating and cooling of the jacketed kettle. Another procedure is to start with only a part of the batch in the kettle; and after the reaction has started and the liberated heat of the reaction has caused an increase of the temperature of the kettle content, additional cold monomer emulsion or water is gradually added to keep the temperature at the desired level. The duration of the polymerization process depends on the temperature employed and the degree of conversion desired and is usually between 18 and 30 hr. at 45 to 70°C. The aftertreatment of the polymer emulsion thus obtained can be performed in many ways according to the end use to which the polymer is put (see page 863).

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[1] Ger. 254,672.

Whereas in bulk and in solution polymerization only catalysts and solvents, respectively, are present besides the monomers, an emulsion polymerization requires a number of additional ingredients for a successful operation. There is first the emulsifying agent, which serves to produce the finely dispersed monomer particles of the emulsion. A large patent literature describes substances that show specific advantages for certain monomers under prevailing reaction conditions. The most commonly used are the water-soluble soaps of long-chain fatty acids (*i.e.*, ammonium oleate), sulfated long-chain alcohols (*i.e.*, sulfated oleyl alcohol), and salts of aliphatic and aromatic sulfonic acids (*i.e.*, sodium naphthalene sulfonate). More recently, aliphatic amines having at least six C atoms or acid salts of them[1] and certain synthetic and natural high polymers have been suggested as emulsifiers. Examples are polyvinyl alcohol,[2] polyacrylamides and polyacrylates,[3] water-soluble polyvinyl ethers,[4] phenolic and urea resins,[4] reaction products of aliphatic alcohols or alkylated phenols with ethylene oxide,[5] methyl cellulose, cholesterin, and saponin. The reaction is most efficiently catalyzed by water-soluble peroxidic compounds, of which hydrogen peroxide, urea peroxide, potassium persulfate, and sodium perborate are preferentially employed. The presence of hydrocarbon-soluble catalysts of the benzoyl peroxide type often results in the formation of a certain amount of lumps, thus restricting their usefulness for the usual type of emulsion polymerization. Also, it is advisable to work in a nitrogen atmosphere, since it is known that the oxygen in the air may retard an emulsion polymerization for a considerable period of time.

Many emulsions of monomers are not too stable and break during the course of the reaction. In order to prevent this, stabilizers and buffering agents must be added. Natural or synthetic protective colloids (*e.g.*, casein, glue, albumin, starch, methyl-celluloses, and polyvinyl alcohol) act as stabilizers, and normal buffering agents (*e.g.*, phosphates

[1] U. S. 2,305,025.

[2] Brit. 444,257; Fr. 798,036.

[3] U. S. 2,120,933; U. S. 2,133,257; Brit. 444,257.

[4] Fr. 798,036; 801,034.

[5] U. S. 2,222,967.

and carbonates, etc.) keep the pH of the emulsion within the desired range. In order to impart specific properties to the polymer, modifiers may be placed in the emulsion before the polymerization is started. It is sometimes necessary to avoid cross linking or branching of the polymer especially if dienes are polymerized or copolymerized. It has been found that chlorinated hydrocarbons, mercaptans, diazo-aminoaryl compounds[1] disulfides,[2] and dixanthates[3] will achieve this purpose. Recently it was also observed that most of these compounds not only act as regulators and modifiers but also retard the reaction, whereas mercaptans with more than six C atoms exert only a regulating effect on the polymer.

After the emulsion polymerization has progressed to the desired degree of conversion, the latex may be used directly or may be coagulated in order to yield solid polymers. If the latex is to be applied directly as a film-forming material or as impregnation for paper, fabric, or leather, plasticizers may be incorporated even at the beginning of the reaction.[4] Also, for coating purposes, a clear solution may be made from the latex if it is concentrated first and then treated with a solvent that is miscible with water.[5] Coagulation of the emulsion can be accomplished in the usual way by addition of electrolytes or by a freezing procedure. Among other methods, the electrophoretic separation of the latex particles[6] and the spraying of the emulsion into a hot gas chamber[7] should be mentioned. Either the coagulated polymer is lumped together (in which case it has to be freed of water by milling on warm rolls and drying under vacuum), or it is precipitated in more or less fine granules, thus simplifying the further drying procedures.

Emulsion polymerization as a continuous operation has been described in the patent literature and has found industrial application. One technic mentioned uses a coiled pipe of such dimensions that at a certain temperature, the monomer emulsion pressed into one end of the pipe polymerizes completely during its passage and latex is continuously removed from the other end.[8] If necessary, a pipe system can be built that is heated to different temperatures at its various sections.[9] Other continuous processes can be carried out in polymerization towers if the monomer has a lower density than water and the polymer a higher one. The monomer emulsion is added at the top of the tower and agi-

[1] U. S. 2,313,233.

[2] U. S. 2,248,107.

[3] U. S. 2,366,328.

[4] Brit. 501,810.

[5] Fr. 797,686.

[6] Fr. 746,969.

[7] Fr. 827,401.

[8] U. S. 2,161,461.

[9] Fr. 847,151.

tated by stirring devices, with turbulence limited to the upper parts of the tower. As the polymerization proceeds and the polymer sinks to the bottom of the tower, new monomer is introduced at the top and latex removed at the base.[1] Instead of one tower, a battery of interconnected reactors can be advantageously used in a similar procedure.[2]

Pearl (Suspension) Polymerization.—The method of emulsion polymerization has proved highly efficient for large-scale production of polymers of high average molecular weight. However, the presence of emulsifiers and other chemicals in the reaction mixture causes these polymers to be not entirely satisfactory in applications involving high optical clarity and outstanding electrical insulating properties. By coagulation of the latex, small amounts of all the ingredients necessary for a successful course of the reaction are occluded inside the agglomerated polymer and cannot be completely removed even by the best washing procedures. The only way to obtain a pure product from an emulsion polymer would be to dissolve and reprecipitate the coagulated polymer repeatedly, a procedure that is not economically feasible in industrial operations. Therefore, a method was sought that, while maintaining the advantages of an emulsion polymerization, would produce polymers of the purity of a bulk polymer. Such a method seems to be the pearl or suspension polymerization, the simple principle of which is to polymerize a monomer while it is kept suspended, in the absence of emulsifiers, in a nonsolvent medium. By adequate agitation, the liquid

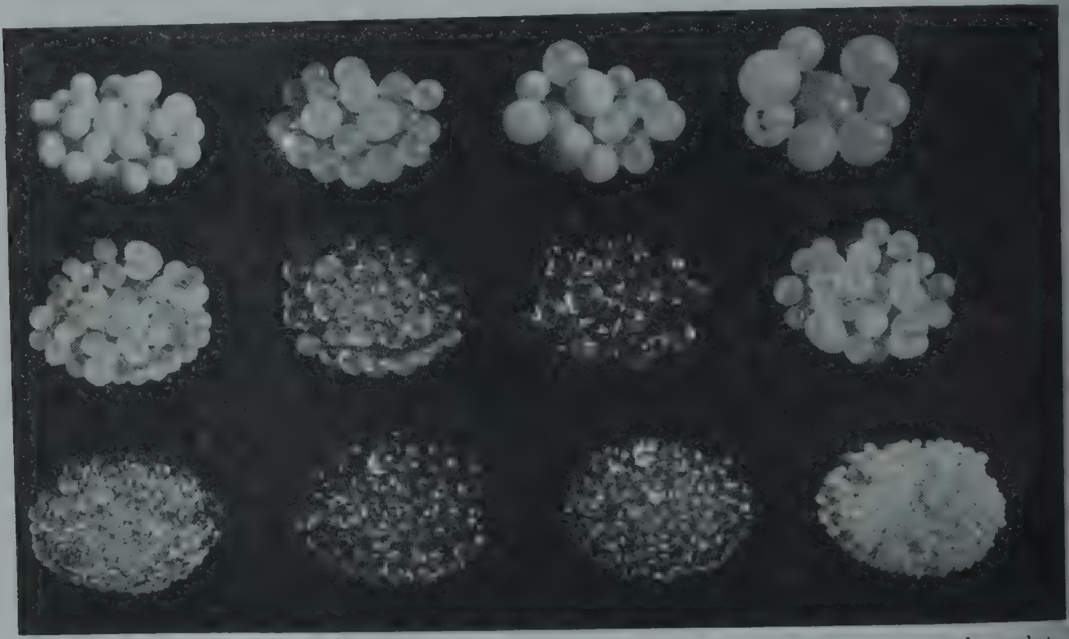

FIG. 25.—Pearl polymers: left to right, methylmethacrylate, vinyl acetate, methacrylate and styrene.

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[1] Fr. 844,023; Ital. 366,669.

[2] Ital. 366,073.

monomer is dispersed into globules of varying size, and after the polymerization is finished the polymer has the form of regularly shaped spheres. In Figure 25 a number of globular polymers are shown (methylmethacrylate, vinyl acetate, methylacrylate, and styrene as arranged from left to right), with particle sizes differing from batch to batch (½ to 3 mm), but almost of the same size resulting from each individual operation. Figure 26 represents a batch of transparent polystyrene pearl polymers. Under proper reaction conditions, polymers of high purity thus can be obtained. These are separated easily from the suspension medium, in a convenient form for storing, shipping, and subsequent molding and extruding operations.

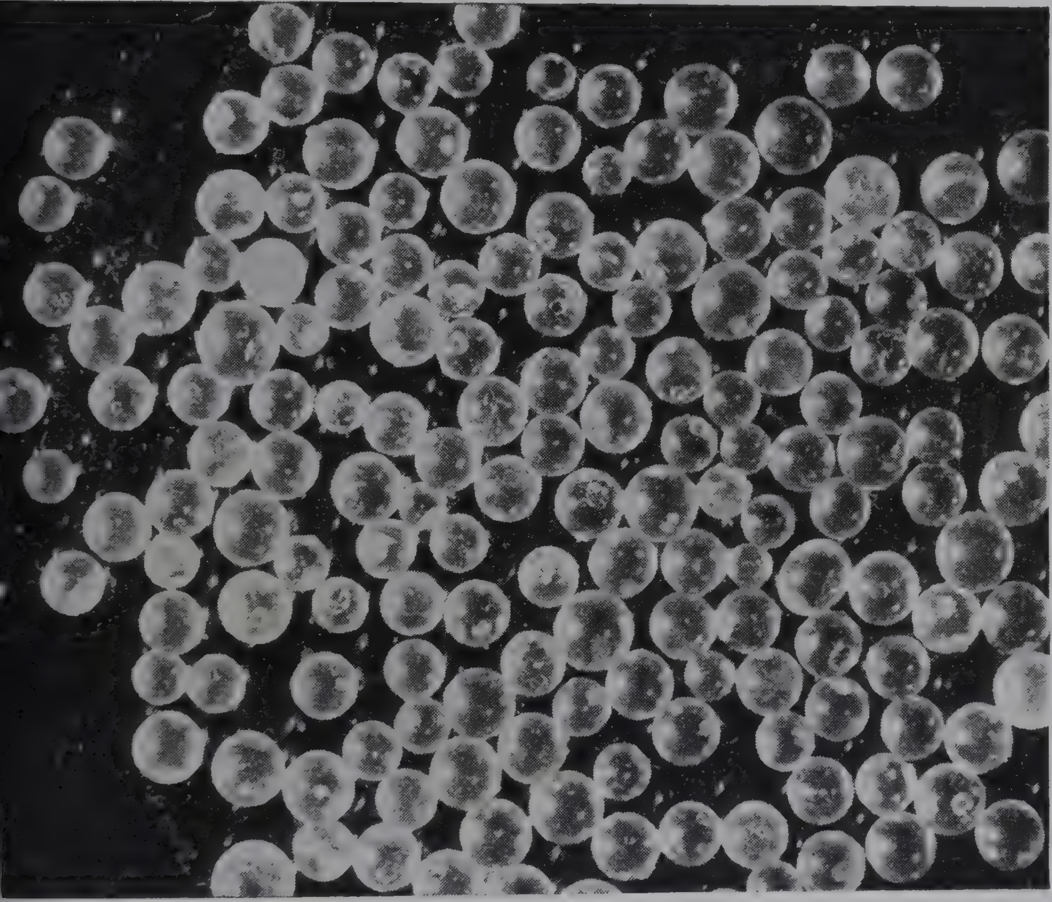


FIG. 26.—Polystyrene pearl polymers.

The reaction itself consists of three distinct phases. During the first one, the inhibition period of the polymerization is overcome, little polymer is formed, and the viscosity of the liquid globules changes only slightly. If during this phase globules collide and coalesce, they are broken up again by the mechanical agitation. After the inhibition period is over more polymer is quickly formed, and it dissolves in the part of the globule which is still monomeric. The globules thus become very viscous and sticky, and if upon collision of two spheres they coalesce, the mechanical agitation is no longer sufficient to separate them. In a brief period all the globular particles will have agglomerated to one big lump. If, however, this sticky period is successfully overcome, the now largely converted spheres are solidified to such an extent that no agglomeration occurs on collision between them. In order to avoid lumping together during the sticky period, it becomes necessary to add small amounts of suspension stablizers, which adhere to the surface of the spheres and protect them from getting into direct contact with one another during the dangerous second phase of the reaction. These stabilizers can be completely removed from the surface of the spheres at the end of the polymerization by adequate washing or floatation processes.

The difference of this method from an emulsion polymerization stands out clearly by the fact that there is no necessity of coagulation since the product already has a form in which it can be handled. Occlusion of foreign matter in the polymer particles can thus be avoided.

Several patents protect the use of stabilizers, which may be of organic or inorganic origin. Among these, gelatin, starch, gum tragacanth, gum acacia, and agar-agar[1] may be mentioned as examples of organic substances; Bentonite, talc, diatomaceous earth, water insoluble inorganic oxides, and hydroxides represent inorganic stablizers. Some high polymeric substances such as polyvinyl alcohol and polymethacrylic acid salts may also be employed for the same purpose.[2] It must be strongly emphasized that the efficiency of stabilizing agents varies with the different monomers and that reaction conditions have to be worked out carefully for each individual case. It is sometimes possible to use the suspension medium containing the stabilizer for a succession of runs after the polymerized pearls have been separated each time.

The catalysts found to be most effective for pearl polymerizations are of the peroxidic type and are soluble in the monomer. This fact, together with data on the energy of activation for the initiation reaction (found to be approximately 26,000 cal./mol) and the relationship of the over-all consumption of monomer and the average molecular weight of the polymer to the square root of the catalyst concentration, points to a bulk

$$\frac{dM}{dt} = \sqrt{c_k} \qquad \bar{P} = \frac{1}{\sqrt{c_k}}$$

polymerization mechanism of the reaction. It seems that pearl polymerization, in effect, constitutes an efficiently cooled bulk polymerization in which the polymerization reaction occurs inside the individual globules. The large amount of liquid surrounding each globule dissipates immedi-

[1] U. S. 2,122,866; 2,108,044; Brit. 427,494; Fr. 780,204; Swed. 85,159.

[2] U. S. 2,067,234; 2,122,886; 2,194,334.

ately any excessive heat built up during the reaction. The fact that one obtains a product of higher average molecular weight and a narrower distribution curve than in bulk polymerization indicates little local overheatings in a suspension polymerization.

The size of the pearls can be altered at will and is determined by balanced conditions of the rate and the efficiency of the stirring; the type and amount of suspension stabilizer used; the speed of the conversion, which in turn depends on temperature and catalyst concentration; the ratio of monomer to the suspension medium; and, finally, the pH of the reaction mixture. The temperature range in which the reaction can be run is limited on the lower side by the temperature at which the catalyst decomposition into radicals starts to influence the speed of the polymerization, and on the upper side by the boiling point of the suspension liquid or the softening range of the polymer formed. It lies, in most cases, between 65 and 90°C.

The comparative conversion speed of a bulk, emulsion, and suspension polymerization and of the average molecular weights of the polymers obtained for similar reaction conditions are presented in Table VII.

TABLE VII.—COMPARISON OF BULK, EMULSION, AND SUSPENSION POLYMERIZATION OF STYRENE

Method	% conversion	Viscosity average molecular weight
Bulk	53.9	40,000
Emulsion	96.6	370,000
Suspension	48.6	67,000

Reaction time, 2 hr.
Reaction temp., 85°C.
Catalyst for bulk and suspension, 0.5% benzoyl peroxide.
Catalyst for emulsion, 0.5% potassium persulfate.

The data indicate that emulsion polymerization converts much faster than either bulk or suspension polymerization and that the average molecular weight of the emulsion polymer is higher than the suspension polymer, which, in turn, exceeds the bulk polymer. Although suspension polymerization proves inferior to emulsion polymerization as far as rate of the reaction and molecular weight of the polymer is concerned, it yields a product of superior purity. Compared with a bulk polymerization, the suspension polymerization produces polymers of equal purity and of slightly higher molecular weight and proceeds without the difficulties of temperature control encountered in the former method.

Pearl polymerization is industrially carried out in closed kettles, provided with a reflux condenser and an efficient stirring mechanism. The finished product is separated from the liquid by sieving procedures, then washed to remove the suspension stabilizer, and finally dried. Sometimes it is necessary to subject the dry pearls to an additional heat treatment in order to convert the last remnants of monomers inside the globules.

Polymerization of Ethylene and Vinyl Derivatives

Ethylene and its mono- and di-substituted derivatives, the vinyl and vinylidene compounds, play an outstanding role in the high-polymer industry. This is mostly due to the cheapness and availability of the monomers which, combined with diversified and valuable properties of the polymers, makes them very attractive for technical applications. A large number of monomeric vinyl derivatives have been prepared and tested for their polymerization possibilities and the properties of their polymers. Out of these the following have been developed for industrial use:

- Polyethylene
- Polyvinyl chloride
- Polyvinyl acetate
- Copolymer of vinyl chloride and vinyl acetate
- Polyvinyl alcohol
- Polyvinyl acetals
- Polyvinyl ketones
- Polyvinyl ethers
- Polyvinylidene chloride
- Polyvinyl carbazol
- Polystyrene
- Polymethacrylates
- Polyacrylates
- Polyindenes
- Polycoumarones
- Polyisobutylene
- Allyl polymers

POLYETHYLENE

$$\cdots\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}\cdots$$

A polymer that became of prime industrial importance during the last decade is obtained by the polymerization of ethylene at high pressures and elevated temperatures. The first attempt to polymerize ethylene at 70 atmos. pressure and at 300°C. led only to liquid products of an average molecular weight of about 3,000. Later development of the process resulted in the preparation of tough and flexible solid polymers, ranging in molecular weights from 10,000 to 100,000. The polymerization reaction is carried out in high-pressure autoclaves at 1,500 atmos. pressure and at temperatures varying from 150 to 250°C. Oxygen in small percentages (0.08 per cent) catalyzes the reaction effectively, though the amount added has to be controlled rigidly in order to prevent explosion of the highly compressed gas. The reaction is strongly exothermic, and effective cooling systems must be installed to keep the temperature and pressure at the desired level. Attempts to polymerize ethylene in emulsion at about 300 atmos. and about 200°C. have also

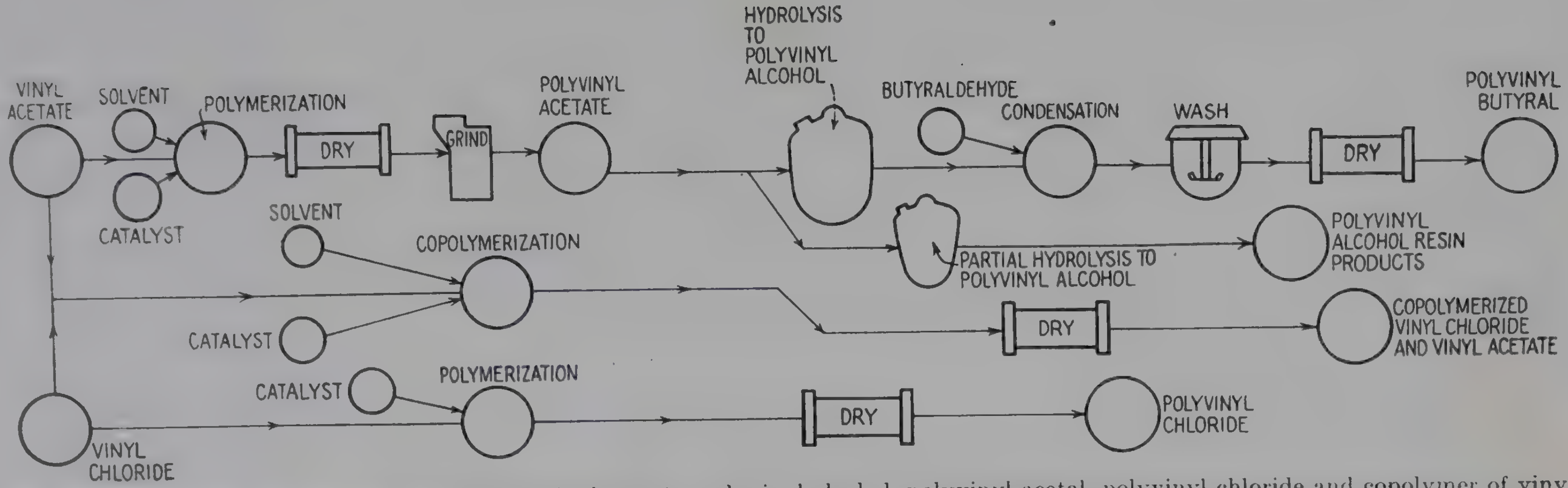

VINYL ACETATE
SOLVENT
CATALYST
POLYMERIZATION
DRY
GRIND
POLYVINYL ACETATE
HYDROLYSIS TO POLYVINYL ALCOHOL
BUTYRALDEHYDE
CONDENSATION
WASH
DRY
POLYVINYL BUTYRAL
PARTIAL HYDROLYSIS TO POLYVINYL ALCOHOL
POLYVINYL ALCOHOL RESIN PRODUCTS
SOLVENT
COPOLYMERIZATION
CATALYST
DRY
COPOLYMERIZED VINYL CHLORIDE AND VINYL ACETATE
CATALYST
POLYMERIZATION
DRY
POLYVINYL CHLORIDE
VINYL CHLORIDE

FIG. 27.—Flow sheet for the production of polyvinyl acetate, polyvinyl alcohol, polyvinyl acetal, polyvinyl chloride and copolymer of vinyl chloride-vinyl acetate.

been successful. The molecular weight of the polymer can be controlled by the chosen conditions of the process. An increase in pressure generally yields products of higher molecular weight, whereas an increase in temperature or concentration of the catalyst tends to lower the degree of polymerization. X-ray investigations of the polymer reveal the presence of a certain degree of crystallinity; the proportion of the crystalline domains in a sample depend upon its thermal history. Mechanical stretching of fibers and films leads to highly oriented products. *Polythene* possesses an inherent flexibility and does not become brittle even at −40°C. A completely amorphous polyethylene can be made by heating the polymer up to its softening point and then quenching it down to room temperature.

The short softening range lies between 110 to 115°C., above which the solid changes to a more or less viscous fluid, depending on the molecular weight of the polymer. Polythene is very resistant against acids and bases and also against most of the conventional solvents. It dissolves at about 80°C. in chlorinated and aromatic hydrocarbons. On cooling, it precipitates out of the solution.

This tough and translucent material is put to many industrial uses, but its outstanding electrical properties make it particularly valuable for insulation in high-frequency equipment. The ready flow of the polymer above its softening range makes molding and extruding relatively easy, and many types of polythene-insulated coils and sockets, low-loss cables, and condensers are on the market. Films and coatings on paper or fabric are made on calenders and prove to be highly impermeable to fumes and water vapor. Fibers and monofilaments made from polythene are used for screens and commercial filter cloth.

POLYVINYL CHLORIDE

Vinyl chloride is produced industrially by two processes:

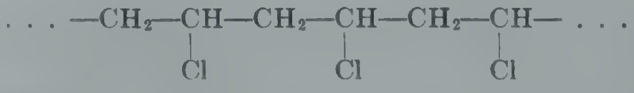
1. By direct addition of HCl to acetylene

$$CH{\equiv}CH + HCl \xrightarrow{HgCl} CH_2{=}CHCl$$

2. By controlled chlorination of ethylene and subsequent removal of HCl

$$CH_2{=}CH_2 + Cl_2 \rightarrow CH_2Cl{-}CH_2Cl \xrightarrow{-HCl} CH_2{=}CHCl$$

The polymerization of the gaseous monomer (b.p., 13.9°C.) is usually performed in emulsion, and the polymer is obtained in the form of a fine powder.[1]



$$\ldots{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}\ldots$$

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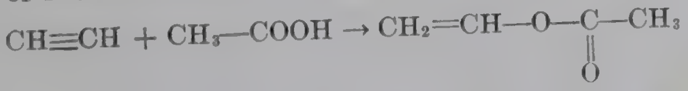
[1] U. S. 1,983,949.

The products so obtained are only difficultly soluble, and elevated temperatures and special solvents such as chloronaphthalene, dibutyl phthalate, tricresyl phosphate, and benzyl benzoate must be employed. In order to achieve better solubility in a larger number of solvents, the polymers are often subjected to further treatment, which consists in an afterchlorination,[1] a treatment with acids,[2] or milling. Increased solubility of the polymer is also attained by solution polymerization at high pressures and temperatures.[3] Polyvinyl chloride is insoluble in its own monomer.

Polyvinyl chloride can be used for molding and extruding purposes. The temperature employed in these operations varies in accordance with the softening range of the polymer, which, in turn, is dependent upon its chlorine content. Normal polyvinyl chloride contains 53 to 55 per cent chlorine and softens at approximately 80°C., whereas strongly afterchlorinated material with a content of 68.5 per cent chlorine softens only at about 140°C.[4] All extruding and molding operations have to be carried out, however, below the temperature at which the polymer begins to decompose (approximately 140 to 160°C.). In order to improve the flow properties of the polymer at these lower temperatures, it is often necessary to add plasticizers, which can be incorporated on hot rolls up to 70 per cent of the total weight. Such highly plasticized polyvinyl chlorides are of rubbery consistency and have found widespread use in applications where elastic properties are needed in addition to good resistance to chemicals, molds, and weather. For other industrial uses, moderately plasticized polyvinyl chloride is rolled out on calenders in the form of foils and sheets or extruded into pipes and small tubes. Polyvinyl chloride is not inflammable and can therefore be worked with open flames, thus allowing easy joining and welding operations. Fibers and yarns of afterchlorinated polyvinyl chloride have also been developed and have served for the preparation of filter cloth, fishing nets, and similar purposes where resistance to acids, alkalies, and molding is of importance.

POLYVINYL ACETATE

Vinyl acetate is formed by the addition of acetylene to acetic acid in the presence of mercuric salts.



$$CH\equiv CH + CH_3\text{—}COOH \rightarrow CH_2\text{=}CH\text{—}O\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_3$$

The monomer can be polymerized in solution, in emulsion, or in sus-

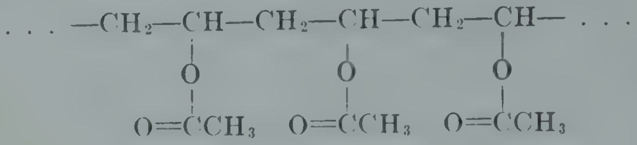
[1] U. S. 2,080,589; Brit. 401,200; Fr. 755,048.

[2] Ger. 647,116.

[3] Brit. 377,653; Fr. 709,562.

[4] Fr. 828,077.

pension. According to the method of polymerization chosen and to the particular conditions of the reaction, polymers of varying average molecular weight are obtained that differ appreciably in their properties.



$$\ldots -CH_2-\underset{\substack{|\\ O\\ |\\ O=CCH_3}}{CH}-CH_2-\underset{\substack{|\\ O\\ |\\ O=CCH_3}}{CH}-CH_2-\underset{\substack{|\\ O\\ |\\ O=CCH_3}}{CH}- \ldots$$

Before polymerizing vinyl acetate, the monomer must be freed of metal and sulfur compounds which inhibit or retard the polymerization and are among the main reasons for a low-molecular-weight product. Acetaldehyde may be present from the preparation of the monomer and, when found in amounts of 0.5 per cent or more, appreciably decreases the average molecular weight of the polymer. In solution polymerization, the choice of the solvent very greatly influences the average molecular weight of the polymer obtained. In contrast, the polymerization degree of a product prepared by emulsion and suspension polymerizations is controlled preponderantly by the temperature and the amount of catalyst added.

Polymers having a number-average molecular weight between 50,000 and 100,000 are soluble in a wide range of solvents, except water, benzene, and aliphatic hydrocarbons. The higher the molecular weight the more difficultly soluble they become. Equally dependent on molecular weight is their behavior at increasing temperature. Low-molecular polymers begin to flow between 30 and 40°C., but products of an average molecular weight of approximately 100,000 become rubbery at temperatures of about 100°C. They decompose at 200°C., splitting off acetic acid and leaving an insoluble and infusible resin as a residue. Their behavior both in solvents and at higher temperatures indicates that either branching or cross linking of the chain molecules may have taken place during the formation of high-molecular-weight polymers.

These properties of polyvinyl acetate limit its usefulness for molding and extruding operations. However, the facts that polyvinyl acetate is compatible with nitrocellulose, exhibits a strong tendency to adhere to glass and metal surfaces, and has a satisfactory light stability assure a substantial market for all grades. Another field of application is that of adhesives for use in the textile and leather industry, where the polyvinyl acetate is employed mainly in the form of aqueous emulsions (latex). Polyvinyl acetate is also used in the production of safety glass, in which it serves as an interlayer and adhesive between two glass plates. Most important for industry is the property of polyvinyl acetate to undergo hydrolysis partly or completely, and thus serve as a starting material for a whole series of polyvinyl alcohols and polyvinyl acetals.

COPOLYMER OF VINYL CHLORIDE-VINYL ACETATE

A series of copolymers of these two monomers can be prepared that differ in solubility, molding characteristics, and chemical stability according to the relative proportions of the monomers used and the average molecular weight obtained. The materials that are most important industrially contain between 85 and 95 per cent vinyl chloride and have an average molecular weight of 10,000 to 30,000. The polymerization procedure can be carried out in either solution or emulsion, depending on the final use to which the copolymer is put. If a completely transparent product is desired, a polymerization in solution, which may be carried out as a continuous process, is preferred. According to this procedure, the monomers are placed in a mixture of solvents that, while dissolving the monomers completely, acts as precipitants for the polymer. In this way, the polymer formed can be continuously removed from the reaction mix, and new monomer and solvent mixture may then be added to restore the original proportions. The vinyl chloride-vinyl acetate copolymers so obtained show a narrower distribution curve than those resulting from a straight solution copolymerization. The reason for this seems to be that the low-molecular-weight copolymers formed remain dissolved in the solvent mixture, and thus a partial fractionation of the precipitated copolymer is automatically achieved.

For many applications, however, the clarity of the polyvinyl chloride-acetate is not essential, because plasticizers and coloring matter must be added in any case in order to make the product comply with particular specifications. For this purpose, the emulsion-polymerization method serves best for the production of the copolymer, and often the latex obtained can be used directly.

The principal technical applications for the copolymers are in the following fields:

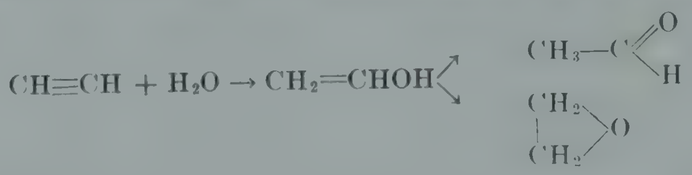
1. Molding and extrusion compounds.
2. Films and coatings.
3. Lacquers.
4. Synthetic fibers.

Products best suited for a particular use are prepared by adjusting the vinyl chloride content and the average molecular weight to the physical and mechanical properties desired. In general, it can be said that a high vinyl chloride content or a high molecular weight is responsible for less solubility and plastic flow and imparts higher resistance to chemicals and temperature.

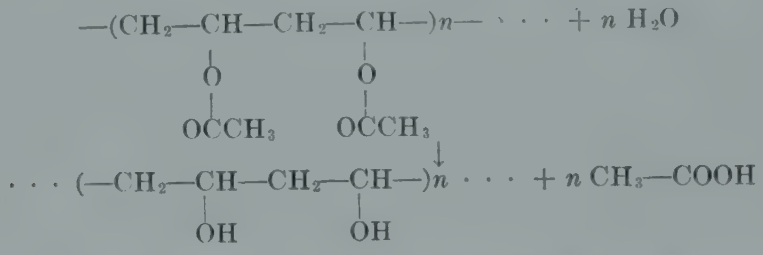
Large quantities of polyvinyl chloride-acetate copolymer are employed for extrusion purposes, for the preparation of self-supporting films, and for coatings on paper and fabric. The dielectric characteristics of the copolymers permit their use as insulators for low-voltage wires and similar extruded electrical equipment. The films have found wide application in industry, for either packaging or the production of artificial leather and raincoats. If a copolymer solution is spun through fine spinerets, the solvent evaporates, and filaments that can be twisted and made into yarns are formed. Although X-ray studies of such fibers do not show appreciable orientation, their strength and elasticity can be greatly enhanced by stretching them along their fiber axis. Fabrics woven from these fibers are used for decorative and industrial purposes.

POLYVINYL ALCOHOL

The monomer of polyvinyl alcohol, vinyl alcohol $CH_2{=}CHOH$, is an unstable substance that, when formed by addition of water to acetylene, quickly isomerizes and forms acetaldehyde and ethylene oxide.



The only way, therefore, by which polyvinyl alcohol can be obtained is by a hydrolysis of polyvinyl acetate.



$$\begin{array}{c} -(\mathrm{CH_2-\underset{\substack{|\\ O\\ |\\ OCCH_3}}{CH}-CH_2-\underset{\substack{|\\ O\\ |\\ OCCH_3}}{CH}-})n- \cdots + n\,\mathrm{H_2O} \\ \downarrow \\ \cdots\ (-\mathrm{CH_2-\underset{\substack{|\\ OH}}{CH}-CH_2-\underset{\substack{|\\ OH}}{CH}-})n\ \cdots + n\,\mathrm{CH_3-COOH} \end{array}$$

The hydrolysis can be performed in an acid or alkaline medium, and conditions may be fixed in such a manner that either a complete or partial hydrolysis is favored. The structure and the properties of the resulting polyvinyl alcohol are determined by the molecular-weight characteristics of the polyvinyl acetate that serves as the starting material and also by the extent to which the hydrolysis is carried out. Thus, various polymers can be devised that differ from one another mostly in solubility. Polyvinyl alcohol itself is soluble in water and practically insoluble in ordinary organic solvents, whereas polyvinyl acetate is soluble in such solvents and only sparingly dissolves in water. The number of acetyl groups still present in an incompletely hydrolized polyvinyl acetate sample will therefore determine to what extent it will be attacked by organic solvents.

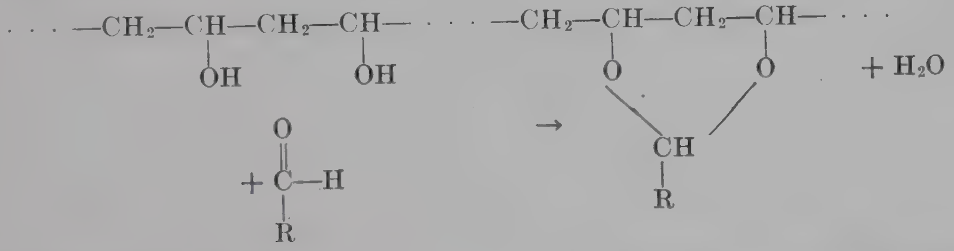
The main applications of polyvinyl alcohol in industry are based on its solubility behavior. For some purposes, its water solubility and the colloidal properties of its solutions are stressed; for other uses, the resistance of polyvinyl alcohol to organic solvents (and especially oils and grease) is of greatest importance. Water solutions of polyvinyl alcohol act as emulsifying vehicles for many hydrophobe liquids and are employed as such in the textile and printing-ink industries. Water-soluble films which can be easily washed off are sometimes desired for temporary protective coatings.

The sensitivity of polyvinyl alcohol films and molded or extruded articles to the dissolving action of water decreases their usefulness for many applications. In order to render the polyvinyl alcohol less soluble or even insoluble in water, it can be treated with formaldehyde or tanning agents,[1] ferric chloride, chromate and bichromates,[2] and cuprammonium hydroxide.[3] For the same purpose, it can also be reacted with dibasic acids, dialdehydes, and dimethylolurea.[4]

Polyvinyl alcohol can be plasticized with water, glycols, or glycerol. It has a rubbery consistency if enough plasticizer is incorporated, and can be used for the production of oil- and greaseproof sheets and hoses.

POLYVINYL ACETALS

The condensation of polyvinyl alcohol with aldehydes leads to the formation of polyvinyl acetals.



The acetals can be made directly from the polyvinyl acetate by carrying out the hydrolysis and condensation steps in one operation.

The properties of the resulting materials depend on

1. The average molecular weight of the polyvinyl acetates used.
2. The amount of acetyl groups hydrolyzed.
3. The degree of acetal formation.
4. The nature of the aldehyde employed for the condensation.

The changes that can be made by adjusting the hydrolysis and condensation conditions, by choosing the starting polyvinyl acetate and the aldehyde offer the possibility of preparing polymers whose properties will correspond to given specifications. Generally, it has been found that the viscosity of polyvinyl acetals in solutions is greater than that of the polyvinyl acetates from which they are made. The length of the hydrocarbon chain of the aldehyde used for the reaction greatly influences the solubility and the heat-softening characteristics. The longer the chain the more easily soluble becomes the polyvinyl acetal but the lower is its softening range. For example, of the two commercially produced acetals, in which the aldehyde components are formaldehyde and butyraldehyde, respectively, the first one is quite resistant to solvents and has a softening range of 160 to 170°F., whereas the polyvinylbutyl acetal is soluble in many organic solvents and has a heat-distortion range of 115 to 140°F.

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[1] Ger. 526,497.

[2] Fr. 807,042.

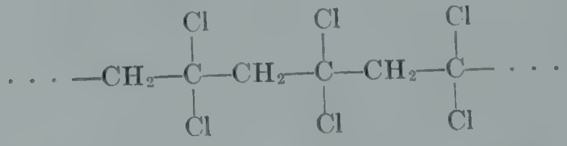
[3] U. S. 2,130,212.

[4] U. S. 2,169,250; Fr. 852,613.

The industrial importance of these polymers is due to the fact that they combine the qualities of toughness, adhesiveness, and moisture insensibility with excellent low-temperature flexibility and shock resistance. For some uses, however, the softening ranges of the normal polyvinyl acetals are too low, and the materials are also too readily attacked by solvents. In a recent development, the addition of certain substances introducing a number of cross links into the thermoplastic polymer has resulted in the formation of polyvinyl acetals that show decreased solubility and better temperature resistance than the straight-chain polymers. The amount of cross linking may reach such an extent that the product becomes practically insoluble. The processing, compounding, and final curing of such materials can be satisfactorily performed on normal rubber equipment.

Polyvinyl acetals are used as insulators for wire coatings, for the impregnation of paper and fabrics, for the production of flexible molded and extruded articles, and as interlayers in safety glass. In the last application, they are superior to any other material thus far tried.

POLYVINYLIDENE CHLORIDE



$$\cdots -CH_2-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CH_2-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CH_2-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}- \cdots$$

There are two methods by which the unsymmetrical dichloroethylene, vinylidene chloride, can be produced commercially. The first process is based on the chlorination of acetylene carried out in acetylene tetrachloride (tetrachloroethane). In the presence of ferric chloride, which acts as a catalyst, acetylene and chlorine combine at 135°C. and yield vinylidene chloride.

$$CH{\equiv}CH + Cl_2 \xrightarrow{FeCl_3} CH_2{=}CCl_2$$

The other method of vinylidene chloride production starts from ethylene which is chlorinated under controlled conditions to yield 1,1,2-trichloroethane. On heating the latter substance in the presence of an alkali

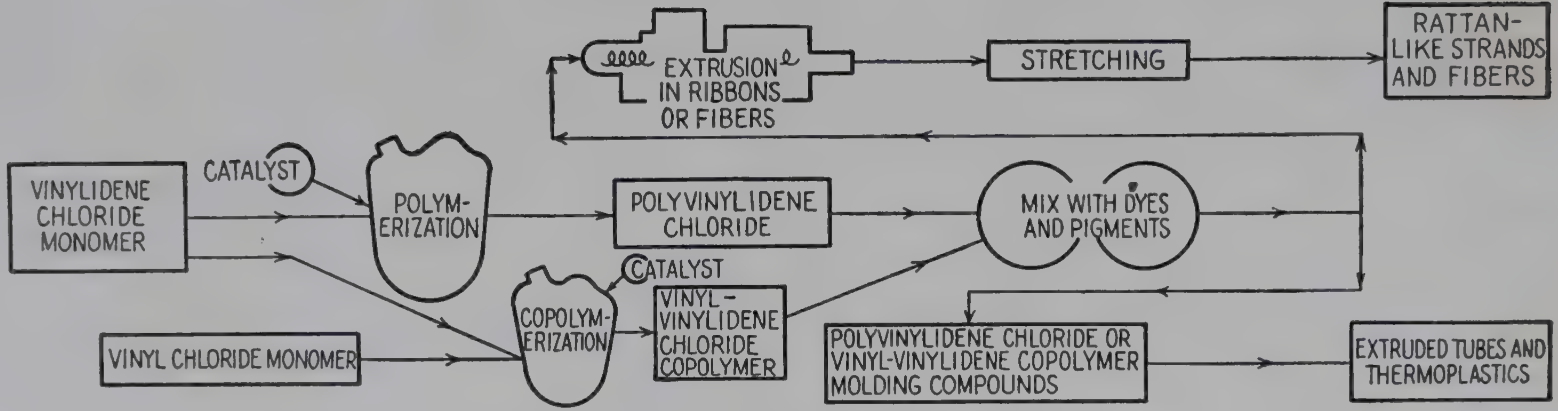
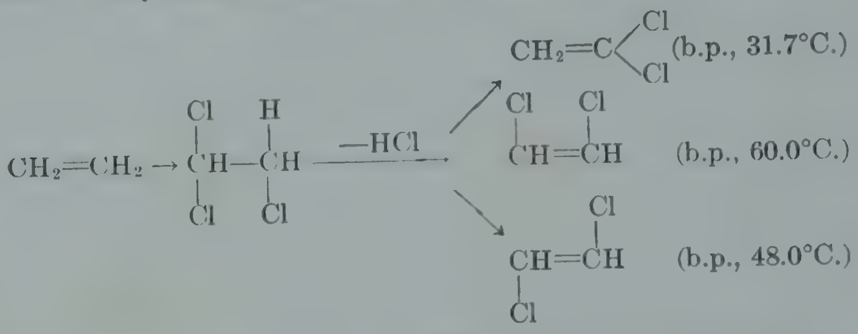

EXTRUSION IN RIBBONS OR FIBERS
STRETCHING
RATTAN-LIKE STRANDS AND FIBERS
VINYLIDENE CHLORIDE MONOMER
CATALYST
POLYM-ERIZATION
POLYVINYLIDENE CHLORIDE
MIX WITH DYES AND PIGMENTS
CATALYST
COPOLYM-ERIZATION
VINYL-VINYLIDENE CHLORIDE COPOLYMER
VINYL CHLORIDE MONOMER
POLYVINYLIDENE CHLORIDE OR VINYL-VINYLIDENE COPOLYMER MOLDING COMPOUNDS
EXTRUDED TUBES AND THERMOPLASTICS

Fig. 28.—Flow sheet for the production of vinylidene chloride resins.

hydrochloric acid is split off, and a mixture of isomeric dichloroethylenes is obtained. They can be separated by fractional distillation.

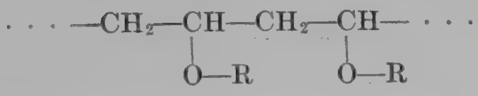

$CH_2{=}CH_2 \rightarrow CHCl{-}CHCl$ (H, Cl above; Cl, Cl below)
—HCl
$CH_2{=}CCl_2$ (b.p., 31.7°C.)
$CHCl{=}CHCl$ (b.p., 60.0°C.)
$CHCl{=}CHCl$ (b.p., 48.0°C.)

Of the three isomers, only the assymmetrically substituted vinylidene chloride polymerizes easily. The polymerization of the monomer can be achieved either under pressure at 30 to 60°C. or in emulsion. Organic peroxides, aluminum chloride, and lead or copper compounds have been found to catalyze the reaction. Oxygen alone also seems to have a catalytic effect, since polymerization of a carefully purified and degassed vinylidene chloride proceeds considerably slower than one carried out in the presence of air. All reactions pass through a characteristically short induction period, and the polymer formed is not soluble in the remaining monomer.

X-ray patterns reveal that the polymer, as it leaves the reaction vessel, is already crystalline to a certain extent. The crystallinity can be greatly increased by stretching the polymer below its softening range, and an orientation of the crystalline regions can ultimately be achieved. The polymer also appears in an amorphous form if it is heated above its melting point and is then rapidly quenched. In the amorphous state, however, the polymer is not stable and, depending on the temperature, reverts back to its crystalline form in time periods ranging from a few seconds to a few days.

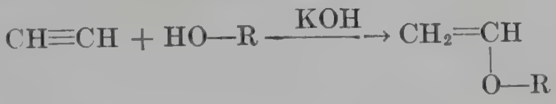
Polyvinylidene chloride softens rather sharply at about 150 to 160°C. but starts to decompose at 130°C., evolving hydrogen chloride. Its solubility is limited to a few solvents, mostly chlorinated hydrocarbons. The difficulties encountered in molding and extruding operations are caused preponderantly by the low decomposition point of the polymer and can be overcome by copolymerizing vinylidene chloride with other vinyl type monomers. The copolymer with vinyl chloride (Saran) softens at 120 to 140°C., has an increased range of solubility, and is more easily compatible with plasticizers than polyvinylidene chloride alone. Saran is commercially produced and is employed as a fiber for the production of fabrics used for cloth, filters, and upholstery. In other applications, use is made of its chemical and solvent resistance for the preparation of gasket material and flexible tubing.

POLYVINYL ETHERS



$$\cdots-CH_2-\underset{\underset{\displaystyle O-R}{|}}{CH}-CH_2-\underset{\underset{\displaystyle O-R}{|}}{CH}-\cdots$$

Vinyl ethers are mostly produced by an addition reaction of acetylene on alcohols with KOH as a catalyst.

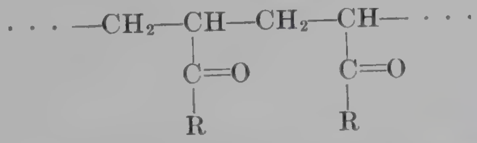


$$CH\equiv CH + HO-R \xrightarrow{KOH} CH_2=\underset{\underset{\displaystyle O-R}{|}}{CH}$$

The polymerization, carried out in bulk or in emulsion, yields polymers of various consistency. The products of low molecular weight are highly viscous oils, whereas higher molecular-weight materials appear as soft resins and hard plastics. Tin tetrachloride and boron trifluoride may serve as catalysts, but peroxides also speed up the reaction under appropriate conditions.

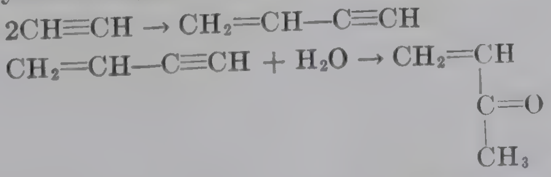
The three polyvinyl ethers that have shown most promise for industrial use are the methyl, ethyl, and isobutyl compounds. They are easily soluble in most organic solvents, the methyl ether showing a characteristic high solubility in cold water and low solubility in hot water. The main application of the polymers is as raw materials for adhesives and laminating agents. Their compatibility with other film-forming natural and synthetic polymeric substances makes them valuable in the formulation of lacquers and varnishes, where they contribute adhesion and flexibility to the film.

POLYVINYL KETONES



$$\cdots-CH_2-\underset{\underset{\underset{\underset{\displaystyle R}{|}}{C=O}}{|}}{CH}-CH_2-\underset{\underset{\underset{\underset{\displaystyle R}{|}}{C=O}}{|}}{CH}-\cdots$$

There are various methods known by which monomeric vinyl ketones can be prepared. The one that is principally employed is based on vinylacetylene, which, in turn, is obtained by dimerization of acetylene. The reaction of vinylacetylene with water in the presence of mercuric sulfate yields vinyl methyl ketone, the most important monomer of the series.



$$2CH\equiv CH \rightarrow CH_2=CH-C\equiv CH$$

$$CH_2=CH-C\equiv CH + H_2O \rightarrow CH_2=\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{C=O}}{|}}{CH}$$

The thoroughly purified ketone can be bulk polymerized to a product of high transparency and clarity.[1] Polyvinyl ketones may be further treated with substances that are known to undergo reactions with the ketonic carbonyl group. Fibers and films of good flexibility have been prepared on a small scale from reaction products of polyvinyl methyl ketone with ammonia and amines.[1]

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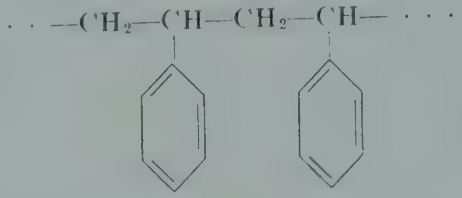
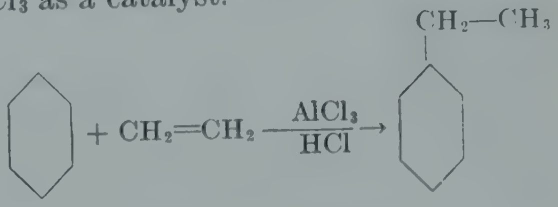
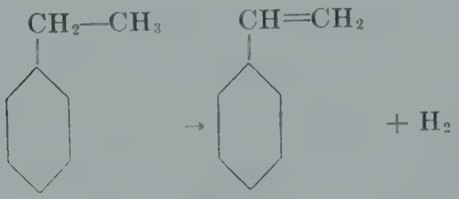
[1] U. S. 2,122,707.

POLYSTYRENE



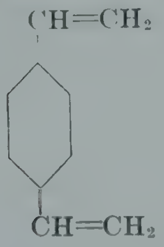
Styrene (vinylbenzene) is commercially produced in large quantities by the dehydrogenation of ethylbenzene which is obtained by the Friedel-Crafts reaction of ethylene and benzene in the presence of hydrogen chloride and $AlCl_3$ as a catalyst.



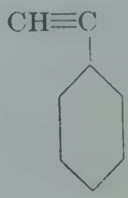


Among other byproducts, (1) divinylbenzene and (2) phenylacetylene are

1.



2.



formed during the reaction. The monomer must be carefully freed from these substances, small amounts of which would cause cross linking and render the polystyrene insoluble.

The polymerization of styrene can be achieved by any one of the known methods of polymerization. If utmost optical clarity is desired, bulk polymerization under mild heat and catalyst conditions is employed. For use as molding powders and coating materials, polymerizations in emulsion and in suspension are carried out. The resulting polymers have varying molecular weights, depending on the reaction conditions employed. The average molecular weight of the polymer, in turn, influences its flow properties and heat resistance.

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[1] Brit. 483,664.

Destructive distillation of the polystyrene above 300°C. yields the monomer and a number of other products that strongly indicate a head-tail structure of the polymer chain. X-ray investigations show that the polymer is amorphous. Stretching and drawing do not seem to produce crystalline or oriented areas, since no typical pattern appears on the diffraction diagram. However, films that are stretched in one or two directions or fibers drawn below the softening range show definite anisotropy in their mechanical and optical behavior. Such materials are commercially produced and are valuable where thin, flexible films of increased tensile strength are desired.

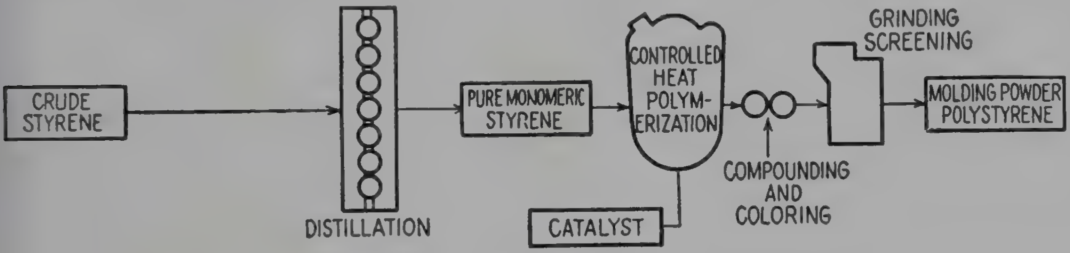
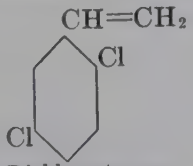


Fig. 29.—Flow diagram for the production of polystyrene resins.

The properties of polystyrene assure this polymer a wide variety of possible applications. Its good flow properties at molding and extruding temperatures permit easy operations and swift production cycles. The dimensional stability of the molded or extruded articles, their transparency, low water absorption, resistance to chemicals, and outstanding electrical properties suggest the use of polystyrene in many industries. A number of factors, though, such as its inherent brittleness, its relatively low softening range (90 to 95°C.), and its inflammability, detract from the value of the polymer. Various suggestions have been made to overcome these shortcomings, and plasticization with chlorinated biphenyls, copolymerization with other olefins or dienes, or the use of ring-chlorinated styrenes seem to show most promise.

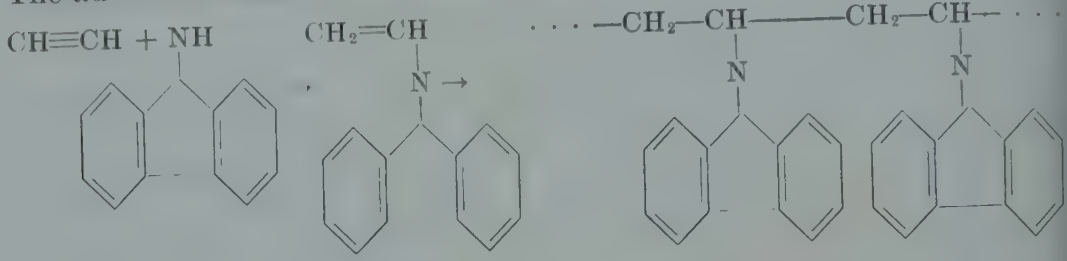


2, 5 Dichlorostyrene

One of the most important applications of styrene is its use in copolymerization with butadiene in the preparation of synthetic rubber of the GR-S type. The production of large quantities of this synthetic rubber during the Second World War brought about a high output of styrene, which became available for other technical uses as the demand for synthetic rubber greatly decreased at the end of the war. Thus, styrene, because of its availability, cheapness, and excellent properties, constitutes one of the most promising vinyl derivatives in the high-polymer industry.

POLYVINYLCARBAZOL

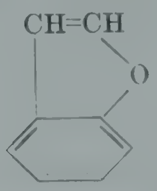
The addition reaction of carbazol on acetylene yields vinyl carbazol.

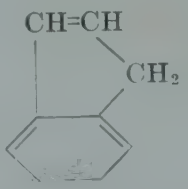


Bulk or dispersion polymerization of the monomer results in the formation of a gray polymer having a softening range from 130 to 150°C. The high working temperature necessary for molding and extruding operations can be efficiently decreased by plasticization of the polymer. An X-ray diffraction diagram of the polymer shows that numerous crystalline regions are present. On stretching, increased crystallinity and orientation can be observed, the drawn sample being anistropic and thus exhibiting greater tensile strength in the direction of the fiber axis.

The electrical properties of polyvinylcarbazol resemble those of polystyrene. This, together with the high heat-distortion temperature of the polymer and its resistance to water, chemicals, and many organic solvents, makes it valuable for application in the electrical industry. Especially in high-frequency work where high-voltage operations must often be conducted at temperatures that exclude the use of polystyrene, the polyvinylcarbazol has found its place and has been frequently employed together with or in the place of mica.

POLYCOUMARONES, POLYINDENES





Indene and coumarone are both found in coal tar, especially in the fractions distilling from 168 to 182°C. Though the two substances can be fairly well separated from the other constituents of the tar and from each other, for commercial purposes the polymerization is directly carried out while the two monomers are still dissolved in the original fraction. Small amounts of sulfuric acid, stannic chloride, or other acidic compounds act as catalysts, and the strongly exothermic reaction has to be controlled for temperature if satisfactory, light-colored resins are sought.

The polymers, which have to be thoroughly freed from solvents and catalysts, have a low degree of polymerization, usually not exceeding average molecular weights of 1,000 to 2,000. The degree of the polymerization determines the softening range of the polymers, and their consistency may accordingly vary from viscous oils to hard, brittle resins melting up to 250°C.

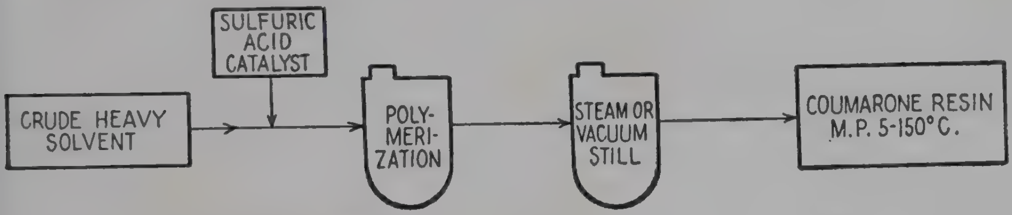
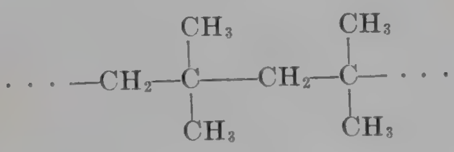


FIG. 30.—Flow diagram for the production of coumarone resins.

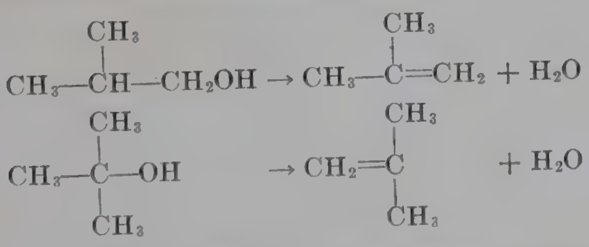
The coumarone-indene polymers are soluble in most organic solvents (except the lower alcohols) and are compatible with many other high polymers, waxes, and drying oils. Their principal applications are as ingredients in lacquer and varnish formulations and in the compounding of rubber. Alcohol-soluble modifications of the polycoumarone-indenes can be obtained by treating the original coal-tar fraction containing the two monomers with phenol. In this manner, some phenolic constituents are built into the chain and impart alcohol solubility to this modified polymer.

POLYISOBUTYLENE



$$\cdots -CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}- \cdots$$

The catalytic dehydration of tertiary or isobutyl alcohol results in the formation of isobutylene in satisfactory yield.



$$CH_3-\overset{CH_3}{CH}-CH_2OH \rightarrow CH_3-\overset{CH_3}{C}=CH_2 + H_2O$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \rightarrow CH_2=\overset{CH_3}{\underset{CH_3}{C}} + H_2O$$

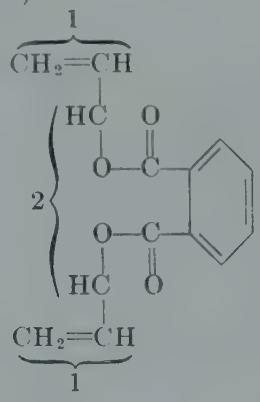
Isobutylene, a gas (b.p. −6°C.), is polymerized in bulk, and the temperature and catalyst conditions of the reaction influence decisively the characteristics of the polymer. Polymerizations carried out at room temperature lead only to low-molecular-weight products. The average degree of polymerization increases as the temperature of the reaction decreases. At a temperature of −78°C., using boron trifluoride, tin tetrachloride, or aluminum chloride as catalysts, high polymers of an average polymerization degree of 3,000 to 4,000 can be obtained. These products are characterized by a high degree of rubberlike elasticity, whereas lower polymers, of an approximate polymerization degree of 1,000, show considerably more plastic flow. Finally, low-molecular-weight polymers of an average polymerization degree of 50 to 100 have the consistency of viscous oils.

The polyisobutylenes, consisting of saturated hydrocarbon chains, show excellent electrical properties and chemical stability. Combined with these characteristics are their elastic and plastic properties, which can be regulated by the proper choice of the average molecular weight of the polymer or by copolymerization of isobutylene with other olefins or dienes. A copolymerization product of isobutylene with a small amount of a diene, *e.g.*, isoprene, has the added advantage of possible vulcanization through the residual double bond of the diene component. Such products are on the market under the name of butyl rubber and have often better aging and ozone-stability characteristics than natural rubber.

Polyisobutylenes have found manifold applications in the rubber and cable industry; they are also used as lubricating oils, as textile finishing and impregnating agents, and for the preparation of self-supporting films and coated fabrics.

ALLYL POLYMERS

Substances containing the allyl group are, in general, difficult to polymerize. In spite of this fact, some allyl polymers have recently been developed and, because of their unusual curing properties, have found interesting commercial application. Allyl chloride, $CH_2{=}CH{-}CH_2Cl$, and allyl alcohol, $CH_2{=}CH{-}CH_2OH$, have been polymerized by themselves[1] but are of far less importance than the allyl esters of organic mono- and dicarboxylic acids. Esters of fumaric acid, sebacic acid, adipic acid, succinic acid,[2] and other organic acids have been prepared on a small scale, and diallyl phthalate is produced on an industrial scale. Owing to their configuration,



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[1] Fr. 853,473.

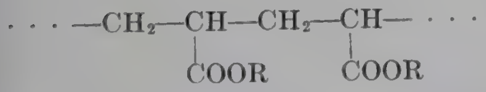
[2] U. S. 2,141,546; 2,155,856; 2,160,940; Brit. 513,221; Fr. 836,029.

the diallyl esters polymerize to heavily cross-linked polymers in which (1) the two vinyl groups of the molecule belong to two different chains and (2) the rest of the diallyl ester molecule provides the linkage between these chains. The polymerization proceeds so slowly at room temperature that uninhibited monomers are stable for many months. In order to achieve higher reaction rates, peroxidic catalysts must be added, and the temperature must be raised to about 70°C.

The conversion of the monomer is carried out by using the bulk-polymerization method. The liquid monomer, containing the catalyst, is cast into a mold, and the polymerization is carried out at moderate temperatures and under slight pressure. During this procedure, the reaction mass becomes increasingly insoluble and heat resisting, and finally the polymer shows the characteristic properties of a thermosetting resin. The cross linking that has taken place during this "curing" process is, however, due to addition polymerization of the two vinyl groups of the molecule. No low-molecular reaction products are split off, as is the case in polycondensations that produce cross-linked and thermosetting polymers. The absence of such volatile substances permits the use of a low-pressure molding technic for the production of large objects of intricate shape.

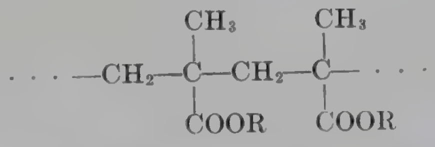
The usual procedure consists in using laminated structures in which porous fabrics or other fibrous matter reinforce the polymeric substances. The laminates are brought into the desired shape and are subsequently cured, just enough pressure being used to maintain the form of the object. Laminates that are based on glass fibers or glass cloth show exceptionally high hardness, tensile strength, and mar resistance.

POLYACRYLATES AND METHACRYLATES



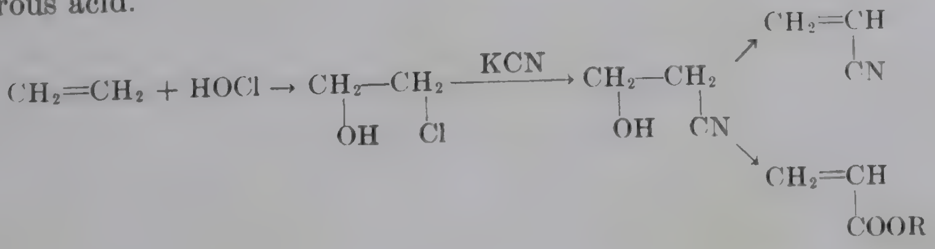
$$\cdots\text{—}CH_2\text{—}\underset{\displaystyle COOR}{\underset{|}{CH}}\text{—}CH_2\text{—}\underset{\displaystyle COOR}{\underset{|}{CH}}\text{—}\cdots$$

and



$$\cdots\text{—}CH_2\text{—}\underset{\displaystyle COOR}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\text{—}CH_2\text{—}\underset{\displaystyle COOR}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\text{—}\cdots$$

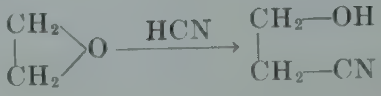
There are three industrially important methods by which monomeric esters of acrylic acid ($CH_2{=}CH\text{—}COOR$) can be prepared, though many other processes have been suggested. The first one starts from ethylene, which is converted to ethylene chlorohydrin by reaction with hypochlorous acid.



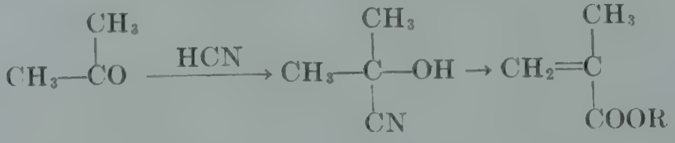
$$CH_2{=}CH_2 + HOCl \rightarrow \underset{\displaystyle OH}{\underset{|}{CH_2}}\text{—}\underset{\displaystyle Cl}{\underset{|}{CH_2}} \xrightarrow{KCN} \underset{\displaystyle OH}{\underset{|}{CH_2}}\text{—}\underset{\displaystyle CN}{\underset{|}{CH_2}} \begin{matrix} \nearrow CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \\ \searrow CH_2{=}\underset{\displaystyle COOR}{\underset{|}{CH}} \end{matrix}$$

Upon reaction with potassium cyanide [or $Ca(CN)_2$], the chlorohydrin yields ethylene cyanhydrin which then can be dehydrated to acrylonitrile or, in a one-step hydrolytic and esterification process, can be converted directly into the acrylic ester.

Another and generally preferred production method for acrylic esters is based on ethylene oxide.

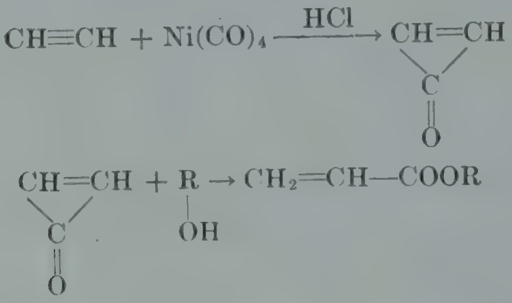


When treated with hydrocyanic acid, ethylene oxide is converted to ethylene cyanhydrin. Esters of the methacrylic acid ($CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}COOR$) are produced in a similar manner from acetone.



$$CH_3{-}\overset{\overset{CH_3}{|}}{CO} \xrightarrow{HCN} CH_3{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH \rightarrow CH_2{=}\underset{\underset{COOR}{|}}{\overset{\overset{CH_3}{|}}{C}}$$

The third method is based on the reaction of acetylene and nickel carbonyl to give the hypothetical cyclopropenone, which, in the presence of an alcohol, gives the corresponding acrylic ester.



In all cases of monomer production, inhibitors must be present at the last stages of the process in order to prevent a premature polymerization of the acrylic or methacrylic esters.

The polymerization of the esters of acrylic and of methacrylic acid can be carried out in bulk, emulsion, or suspension. Care must be taken in the emulsion or suspension polymerization of acrylic esters because of possible hydrolysis of the monomers and polymers. Bulk polymerization of methacrylic esters, if carried out under special precautions, yields polymers of outstanding clarity.[1]

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[1] U. S. 1,710,825; Brit. 261,406; Ger. 446,562.

The polymers of methacrylic esters differ in some respects from those of the acrylic series. They are harder than the corresponding polyacrylates and have a higher softening range. At temperatures of about 250°C., the lower polymethacrylates, *e.g.*, polymethyl methacrylate, depolymerize to the monomers, whereas the polymeric acrylic esters decompose at the same temperature into a number of complex compounds.[1] Finally, the polymethacrylates are stable to alkalies and acids, but the polyacrylates can be hydrolyzed to polyacrylic acid.

The polymeric esters of each of the series show the same trend as far as softening range, hardness, and solubility characteristics are concerned.

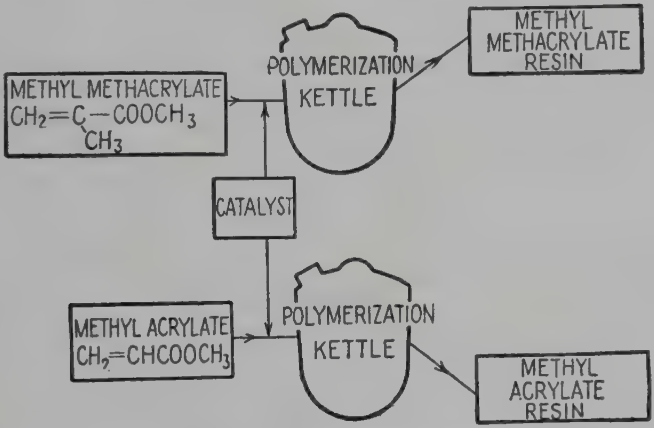

FIG. 31.—Flow diagram for the production of acrylic and methacrylic resins.

The lower esters are generally harder, have higher softening points, but are less soluble in ordinary organic solvents than the esters derived from higher alcohols. For this reason, polymethyl methacrylate, as the lowest in the methacrylic ester series, is singled out for molding and extruding purposes. Copolymerization of methyl methacrylate with ethyl or butyl esters yields materials having a wider range of solubility. It is interesting to note that the polymers of two different esters of the same acid or of two esters of acrylic and methacrylic acid are incompatible with each other but can be copolymerized if the mixed monomers are subjected to polymerizing conditions.

Besides furnishing the plastics industry with one of its most valuable molding compounds, polymethyl methacrylates and its copolymers with other vinyl derivatives are used in the manufacture of foils and lacquers and for coatings on wood, fabric, and paper. Among the desirable properties possessed by such films and coatings is their excellent resistance to weathering and aging. This is due to the fact that the decomposition product of polymethyl methacrylate is the neutral monomer that does not actively support further depolymerization.

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[1] U. S. 2,030,901; Brit. 460,009.

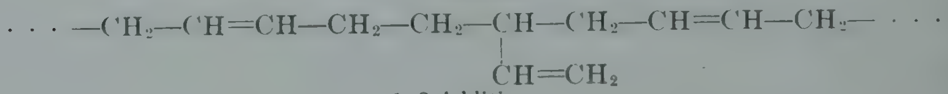
POLYMERIZATION AND COPOLYMERIZATION OF DIENES

Diolefins that serve as monomers for technically important polymerization products are either butadiene itself or derivatives of it. Though other dienes have been suggested for polymerization purposes and are being presently investigated and developed, so far only the members of the polybutadiene group have been produced industrially on a large scale. The first attempts to polymerize a butadiene derivative were made with isoprene (methylbutadiene), since it had been found that rubber is built up from isoprene units. However, the difficulties encountered in producing isoprene economically in large quantities focused the attention of scientific and industrial research on butadiene and on its halogen derivatives. In recent years, the production of butadiene and 2-chlorobutadiene (chloroprene) has become a major industrial process.

BUTADIENE POLYMERS AND COPOLYMERS

$$\cdots\mathrm{-CH_2-CH{=}CH-CH_2-CH_2-CH{=}CH-CH_2-}\cdots$$

1, 4 Addition



$$\cdots\mathrm{-CH_2-CH{=}CH-CH_2-CH_2-\underset{\substack{|\\ CH{=}CH_2}}{CH}-CH_2-CH{=}CH-CH_2-}\cdots$$

1, 2 Addition

In the United States, butadiene is produced industrially either from ethyl alcohol (Carbide and Carbon Chemical Corporation process[1]) or by dehydrogenation of mixtures of butane and butenes as obtained by special oil-cracking procedures. In Germany during the Second World War, it was derived from acetylene by two methods involving (1) the formation of 1, 3-butylene glycol and its subsequent dehydration or (2) the formation of vinylacetylene and its reduction to butadiene.

The polymerization of butadiene can be carried out in bulk or solution at low temperature, using metallic sodium as a catalyst, or in emulsion in the presence of peroxidic or other special catalysts. A variety of products can be obtained; they range in their consistency from viscous oils and rubbery substances of different degrees of hardness and elasticity to solid brittle resins. With the exception of the rubbery materials, which were prepared with metallic Na as catalyst and were used to a certain extent in Germany, none of the butadiene polymers have found significant industrial application. Even the rubbery products were soon superseded in quality and usefulness by the copolymers of butadiene and certain vinyl derivatives.

The copolymers of butadiene with styrene (GR-S type) or with acrylonitrile (GR-N type) were largely developed in the United States during the Second World War and, during the emergency, replaced natural rubber in most of its applications. The conversion of the monomers into the copolymer is achieved by polymerization in emulsion, and the intensive scientific research instigated by these large-scale industrial operations has helped to provide the plastics industry in general with a better control and understanding of this polymerization method.

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[1] Carbide and Carbon process, U. S. Senate Subcommittee Agriculture and Forestry, p. 1258, Washington, 1943; U. S. 2,393,381 (1946).

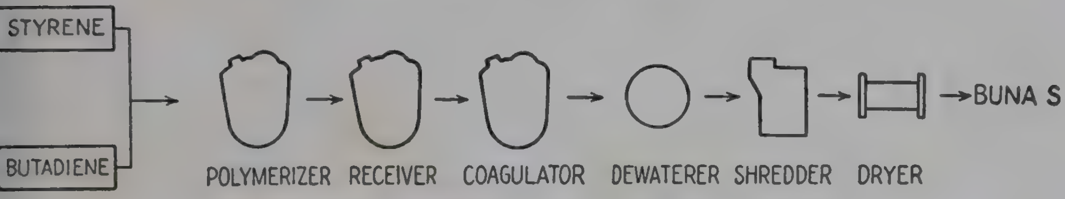
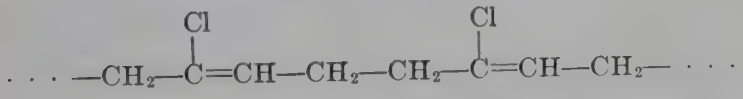


Fig. 32.—Flow diagram for the production of Buna S.

The copolymerization is carried out in stirred autoclaves in a nitrogen atmosphere at temperatures of about 50°C. and in the presence of peroxidic catalysts, emulsion stabilizers, buffering agents, and polymerization regulators, all of which contribute to a smooth reaction procedure and influence the characteristics of the final product. After being freed from remaining monomers, the copolymers may be used directly in the form of the latex, or the latex may be coagulated, and the coagulate washed and dried. Vulcanization of the rubber so obtained is essentially brought about in the same manner as with natural rubber, although the specific time requirements for vulcanization are not so critical.

The properties of the synthetic rubbers vary with the type of monomer used in conjunction with butadiene and with the relative proportions of diene and olefin. In some respects, however, such as abrasion resistance; inertness to chemicals, hydrocarbon solvents, and oils; and resistance to heat and aging, they are equal or superior to natural rubber. However, the latter is still superior in elasticity and resistance to flexcracking.

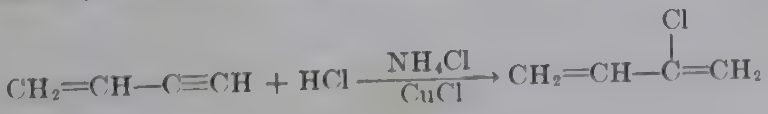
CHLOROPRENE



$$\cdots -CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}=CH-CH_2- \cdots$$

Of all the mono-substituted halogen derivatives of butadiene, chloroprene (2-chlorobutadiene) was the only one to be used for the industrial production of large amounts of synthetic rubber.

The preparation of the monomer starts with acetylene, which, when treated with cuprous chloride is converted to vinylacetylene. In a further reaction, in the presence of cuprous chloride and NH_4Cl, vinylacetylene and hydrochloric acid form chloroprene.



$$CH_2{=}CH{-}C{\equiv}CH + HCl \xrightarrow[CuCl]{NH_4Cl} CH_2{=}CH{-}\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH_2$$

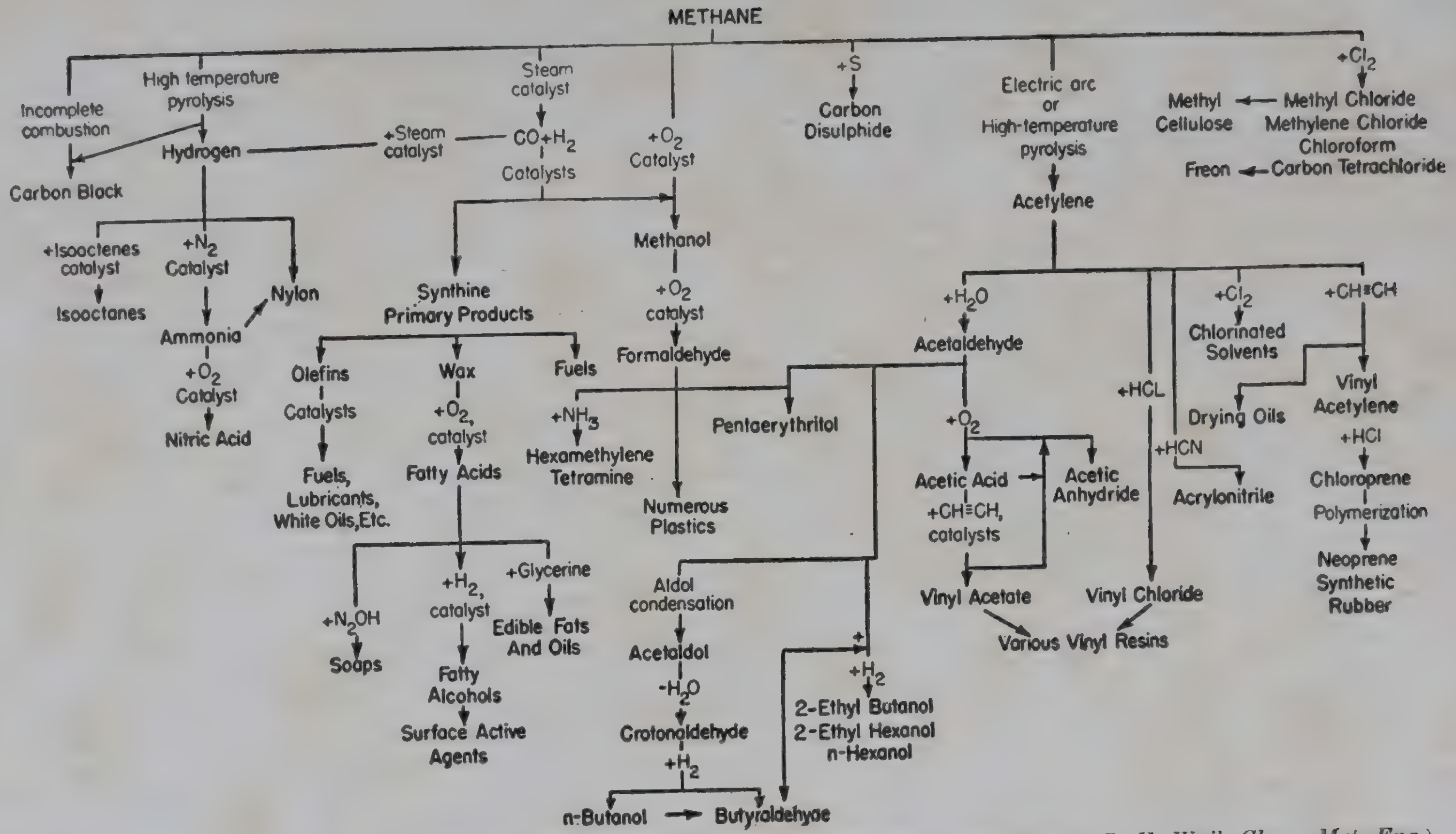
The preferred method for the polymerization of the chloroprene is emulsion polymerization, although bulk and solution polymerization are also employed for the production of special types of the polymer. Depending on the conditions of the reaction, four different forms of the polymer can be obtained. By polymerization in emulsion or by partial polymerization in bulk and solution at room temperature, an α polymer is formed that corresponds in its properties to unvulcanized rubber. If this polymer is subjected to heat, μ polymer is formed which behaves like vulcanized rubber, is heat-resistant, and practically insoluble. This "vulcanization" or "curing" effect is essentially a cross-linking reaction and is accelerated by oxygen and light.

The third type of polychloroprene, together with other polychloroprenes, is formed in a bulk polymerization at elevated temperature and in the absence of oxygen. This β polymer represents an oil and is probably a mixture of low-molecular polychloroprene chains. Finally, ω polymer is sometimes obtained, together with α polymer, and appears as a hard solid resin.

The type of polychloroprene that is industrially produced is the α polymer. It has found widespread application because of some characteristics that make it superior to natural rubber. Its outstanding property is its resistance to oils, heat, and aging, which renders it most valuable for uses where natural rubber fails in these respects. It can be worked on normal rubber-processing equipment. Variations of the characteristics of the polymer, regulating its plasticity and elasticity, curing time, and heat stability, can be achieved by copolymerization of the monomer with another olefin or diene, by the choice of polymerization methods and catalysts, and by the admixture of curing and modifying agents.

APPENDIX 1

METHANE



METHANE
Incomplete combustion
High temperature pyrolysis
Carbon Black
Hydrogen
+Steam catalyst
Steam catalyst
CO+H$_2$
Catalysts
+O$_2$ Catalyst
+S
Carbon Disulphide
Electric arc or High-temperature pyrolysis
Acetylene
+Cl$_2$
Methyl Chloride
Methylene Chloride
Chloroform
Carbon Tetrachloride
Methyl Cellulose
Freon
+Isooctenes catalyst
Isooctanes
+N$_2$ Catalyst
Ammonia
Nylon
+O$_2$ Catalyst
Nitric Acid
Synthine Primary Products
Olefins
Catalysts
Fuels, Lubricants, White Oils,Etc.
Wax
+O$_2$, catalyst
Fatty Acids
Fuels
+N$_2$OH
Soaps
+H$_2$, catalyst
Fatty Alcohols
Surface Active Agents
+Glycerine
Edible Fats And Oils
Methanol
+O$_2$ catalyst
Formaldehyde
+NH$_3$
Hexamethylene Tetramine
Numerous Plastics
Pentaerythritol
Aldol condensation
Acetaldol
-H$_2$O
Crotonaldehyde
+H$_2$
n-Butanol
Butyraldehyde
+
+H$_2$
2-Ethyl Butanol
2-Ethyl Hexanol
n-Hexanol
+H$_2$O
Acetaldehyde
+O$_2$
Acetic Acid
Acetic Anhydride
+CH≡CH, catalysts
Vinyl Acetate
Various Vinyl Resins
+HCL
Vinyl Chloride
+HCN
Acrylonitrile
+Cl$_2$
Chlorinated Solvents
Drying Oils
+CH≡CH
Vinyl Acetylene
+HCl
Chloroprene
Polymerization
Neoprene Synthetic Rubber

FIG. 1 APP.—Methane has become an important source of synthetic organics. (*According to B. H. Weil, Chem. Met. Eng.*)

APPENDIX 2

ETHYLENE

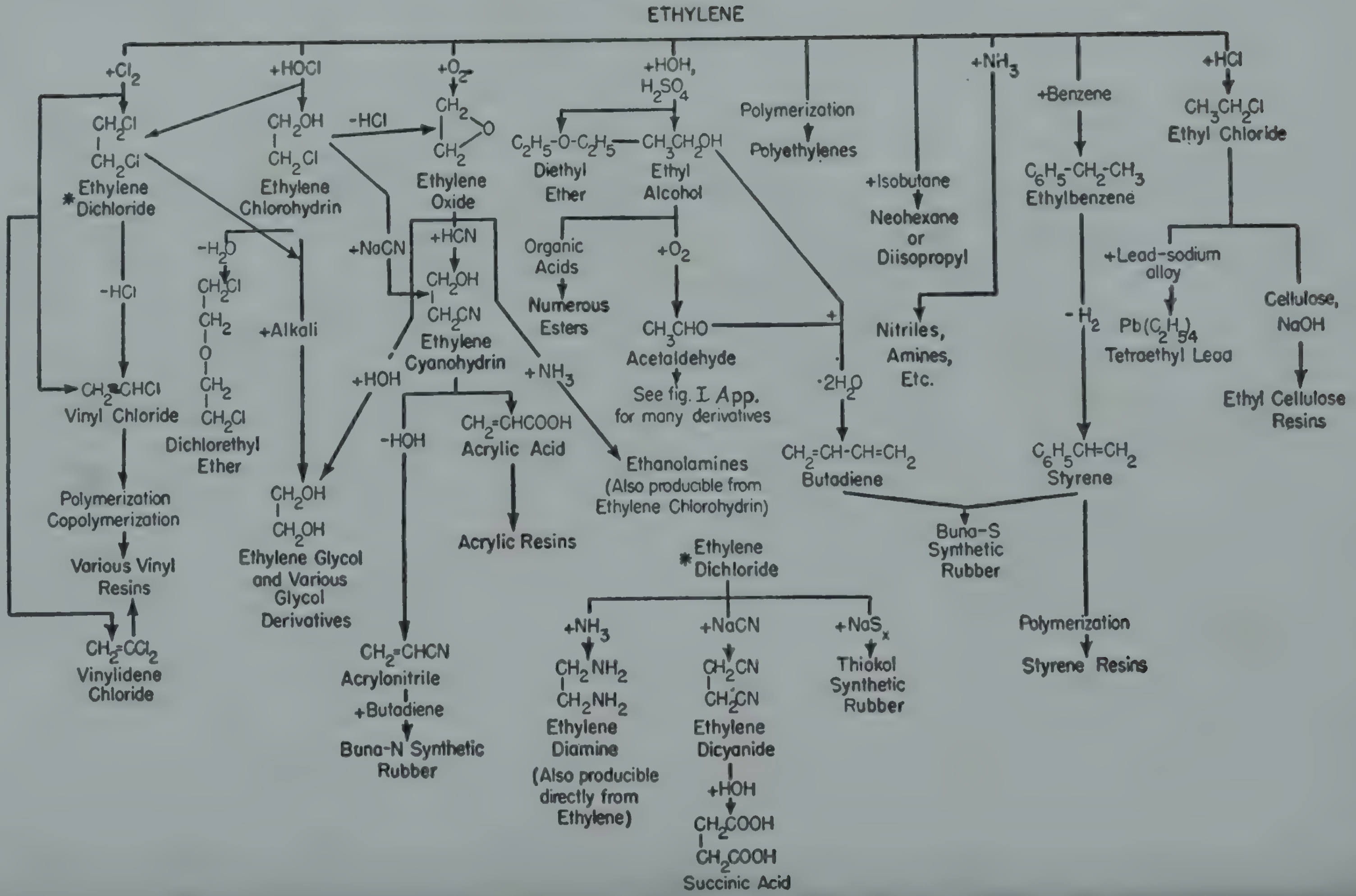

ETHYLENE
+Cl2
CH2Cl
CH2Cl
* Ethylene Dichloride
-HCl
CH2=CHCl
Vinyl Chloride
Polymerization
Copolymerization
Various Vinyl Resins
CH2=CCl2
Vinylidene Chloride
+HOCl
CH2OH
CH2Cl
Ethylene Chlorohydrin
-H2O
CH2Cl
CH2
O
CH2
CH2Cl
Dichlorethyl Ether
+Alkali
CH2OH
CH2OH
Ethylene Glycol and Various Glycol Derivatives
-HCl
+NaCN
+O2
CH2
CH2
O
Ethylene Oxide
+HCN
CH2OH
CH2CN
Ethylene Cyanohydrin
+HOH
-HOH
CH2=CHCN
Acrylonitrile
+Butadiene
Buna-N Synthetic Rubber
CH2=CHCOOH
Acrylic Acid
Acrylic Resins
+NH3
Ethanolamines
(Also producible from Ethylene Chlorohydrin)
+HOH, H2SO4
C2H5-O-C2H5
Diethyl Ether
CH3CH2OH
Ethyl Alcohol
Organic Acids
Numerous Esters
+O2
CH3CHO
Acetaldehyde
See fig. I App. for many derivatives
+
·2H2O
CH2=CH-CH=CH2
Butadiene
* Ethylene Dichloride
+NH3
CH2NH2
CH2NH2
Ethylene Diamine
(Also producible directly from Ethylene)
+NaCN
CH2CN
CH2CN
Ethylene Dicyanide
+HOH
CH2COOH
CH2COOH
Succinic Acid
+NaSx
Thiokol Synthetic Rubber
Polymerization
Polyethylenes
+Isobutane
Neohexane or Diisopropyl
+NH3
Nitriles, Amines, Etc.
Buna-S Synthetic Rubber
+Benzene
C6H5-CH2-CH3
Ethylbenzene
-H2
C6H5CH=CH2
Styrene
Polymerization
Styrene Resins
+HCl
CH3CH2Cl
Ethyl Chloride
+Lead-sodium alloy
Pb(C2H5)4
Tetraethyl Lead
Cellulose, NaOH
Ethyl Cellulose Resins

FIG. 2 APP.—Many important derivatives are commercially produced from ethylene. (*According to B. H. Weil, Chem. Met. Eng.*)

APPENDIX 3

PROPYLENE

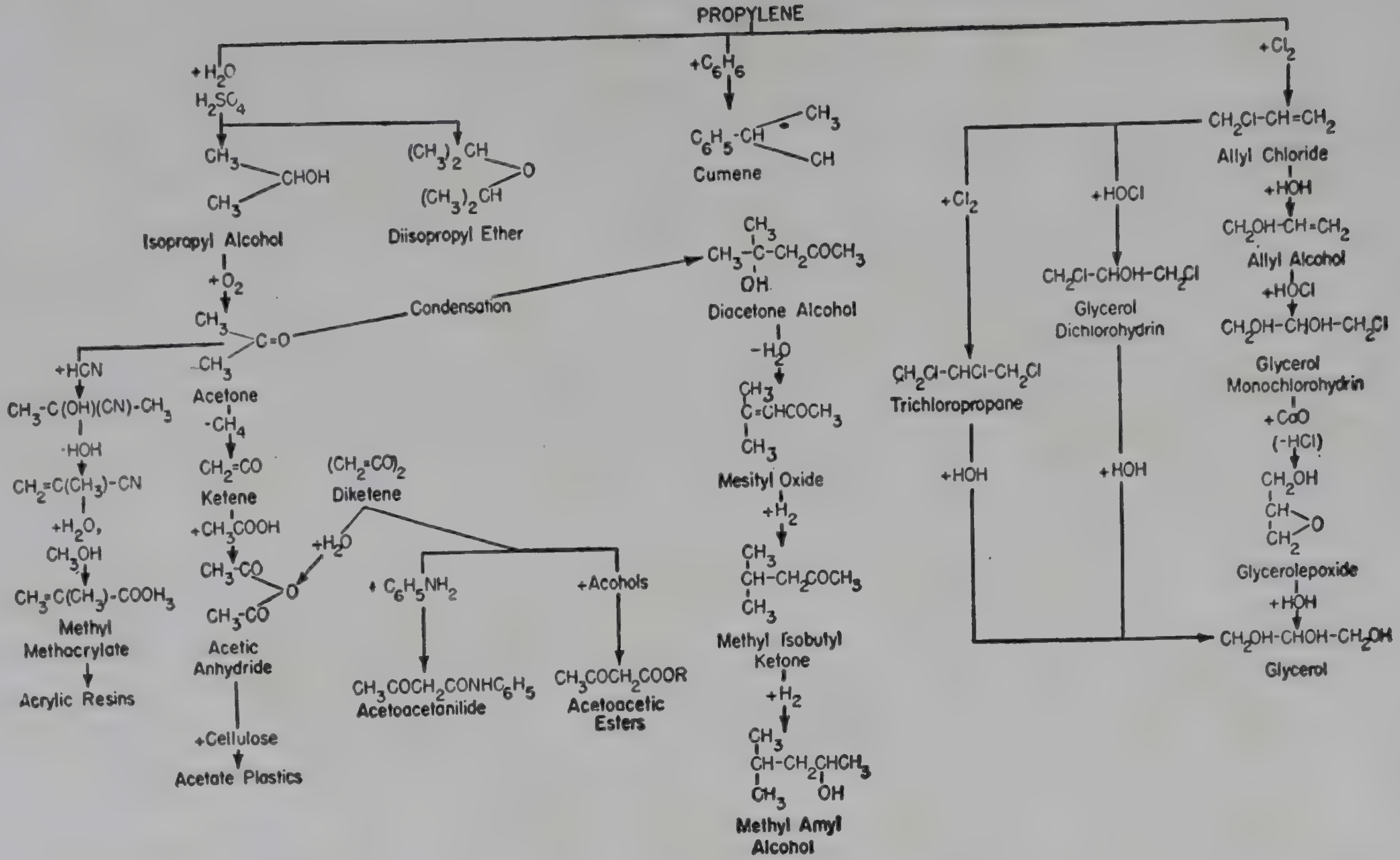

PROPYLENE
+H2O H2SO4
CH3-CHOH-CH3
Isopropyl Alcohol
(CH3)2CH-O-CH(CH3)2
Diisopropyl Ether
+O2
CH3-C=O-CH3
Acetone
Condensation
+HCN
CH3-C(OH)(CN)-CH3
-HOH
CH2=C(CH3)-CN
+H2O, CH3OH
CH3=C(CH3)-COOH3
Methyl Methacrylate
Acrylic Resins
-CH4
CH2=CO
Ketene
+CH3COOH
CH3-CO-O-CH3-CO
Acetic Anhydride
+Cellulose
Acetate Plastics
(CH2=CO)2
Diketene
+H2O
+C6H5NH2
CH3COCH2CONHC6H5
Acetoacetanilide
+Acohols
CH3COCH2COOR
Acetoacetic Esters
+C6H6
C6H5-CH(CH3)CH
Cumene
CH3-C(CH3)(OH)-CH2COCH3
Diacetone Alcohol
-H2O
CH3-C(CH3)=CHCOCH3
Mesityl Oxide
+H2
CH3-CH(CH3)-CH2COCH3
Methyl Isobutyl Ketone
+H2
CH3-CH(CH3)-CH2CH(OH)CH3
Methyl Amyl Alcohol
+Cl2
CH2Cl-CH=CH2
Allyl Chloride
+Cl2
CH2Cl-CHCl-CH2Cl
Trichloropropane
+HOH
+HOCl
CH2Cl-CHOH-CH2Cl
Glycerol Dichlorohydrin
+HOH
+HOH
CH2OH-CH=CH2
Allyl Alcohol
+HOCl
CH2OH-CHOH-CH2Cl
Glycerol Monochlorohydrin
+CaO
(-HCl)
CH2OH-CH-CH2>O
Glycerolepoxide
+HOH
CH2OH-CHOH-CH2OH
Glycerol

FIG. 3 APP.—Propylene is a cheap raw material obtained from the by-product gases of thermal and catalytic cracking. (*According to B. H. Weil, Chem. Met. Eng.*)

APPENDIX 4

Petroleum and Natural Gas

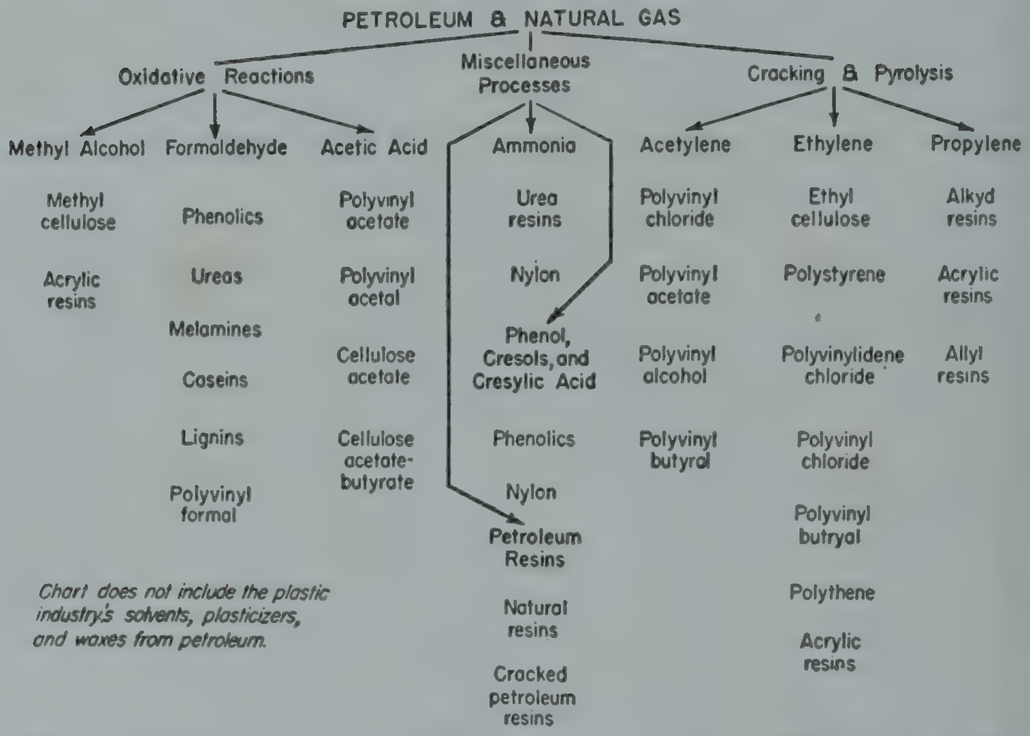

PETROLEUM & NATURAL GAS
Oxidative Reactions
Miscellaneous Processes
Cracking & Pyrolysis
Methyl Alcohol
Formaldehyde
Acetic Acid
Ammonia
Acetylene
Ethylene
Propylene
Methyl cellulose
Acrylic resins
Phenolics
Ureas
Melamines
Caseins
Lignins
Polyvinyl formal
Polyvinyl acetate
Polyvinyl acetal
Cellulose acetate
Cellulose acetate-butyrate
Urea resins
Nylon
Phenol, Cresols, and Cresylic Acid
Phenolics
Nylon
Petroleum Resins
Natural resins
Cracked petroleum resins
Polyvinyl chloride
Polyvinyl acetate
Polyvinyl alcohol
Polyvinyl butyral
Ethyl cellulose
Polystyrene
Polyvinylidene chloride
Polyvinyl chloride
Polyvinyl butryal
Polythene
Acrylic resins
Alkyd resins
Acrylic resins
Allyl resins

Chart does not include the plastic industry's solvents, plasticizers, and waxes from petroleum.

Fig. 4 App.—Basic reactions and their resulting products. (*According to B. H. Weil, Chem. Met. Eng.*)

APPENDIX 5

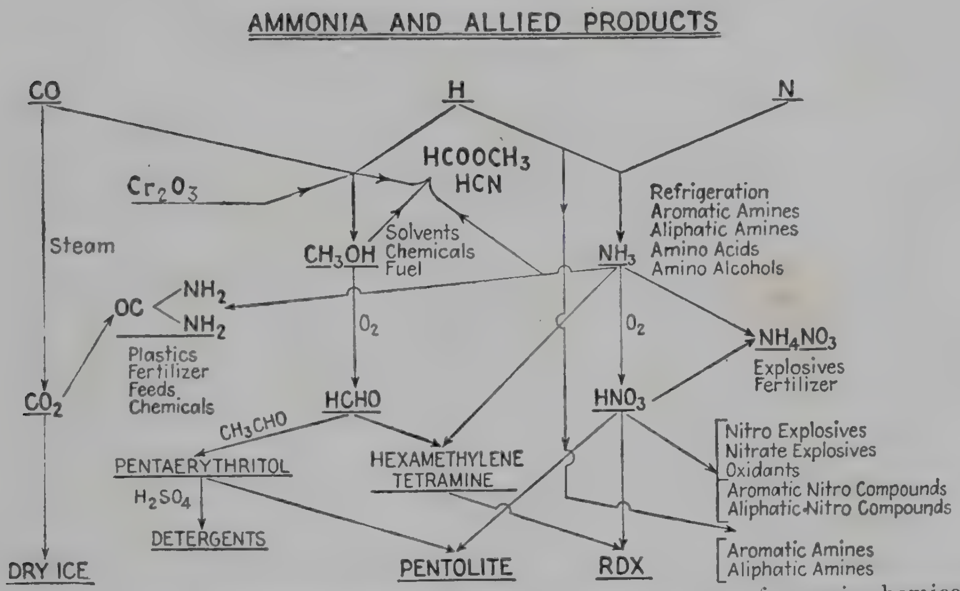

AMMONIA AND ALLIED PRODUCTS
CO
H
N
HCOOCH$_3$
HCN
Cr$_2$O$_3$
Steam
Refrigeration
Aromatic Amines
Aliphatic Amines
Amino Acids
Amino Alcohols
CH$_3$OH
Solvents
Chemicals
Fuel
NH$_3$
OC<NH$_2$ NH$_2$
Plastics
Fertilizer
Feeds
Chemicals
O$_2$
O$_2$
NH$_4$NO$_3$
Explosives
Fertilizer
CO$_2$
HCHO
HNO$_3$
CH$_3$CHO
Nitro Explosives
Nitrate Explosives
Oxidants
Aromatic Nitro Compounds
Aliphatic Nitro Compounds
PENTAERYTHRITOL
HEXAMETHYLENE TETRAMINE
H$_2$SO$_4$
DETERGENTS
Aromatic Amines
Aliphatic Amines
DRY ICE
PENTOLITE
RDX

Fig. 5 App.—A water-gas ammonia plant is an important source of organic chemicals.

APPENDIX 6

HYDROGEN

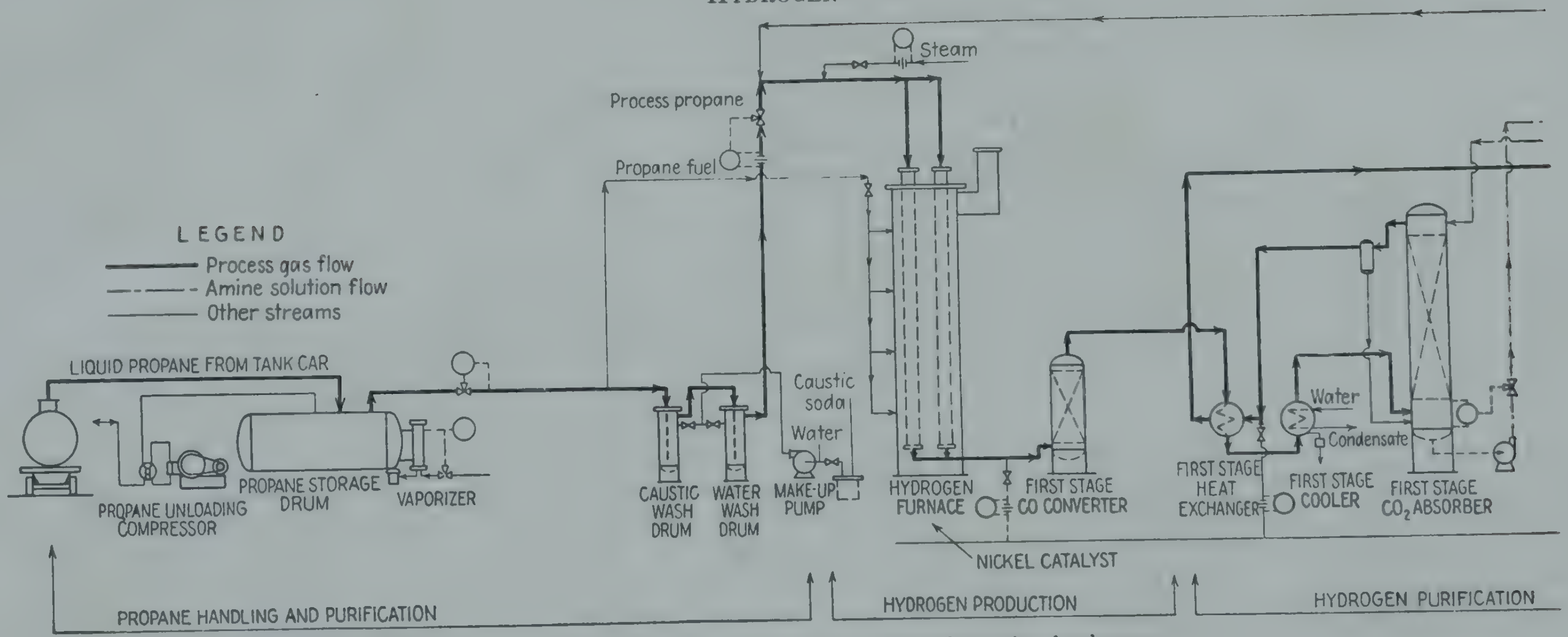

Steam
Process propane
Propane fuel
LEGEND
Process gas flow
Amine solution flow
Other streams
LIQUID PROPANE FROM TANK CAR
Caustic soda
Water
Water
Condensate
PROPANE UNLOADING COMPRESSOR
PROPANE STORAGE DRUM
VAPORIZER
CAUSTIC WASH DRUM
WATER WASH DRUM
MAKE-UP PUMP
HYDROGEN FURNACE
FIRST STAGE CO CONVERTER
FIRST STAGE HEAT EXCHANGER
FIRST STAGE COOLER
FIRST STAGE CO₂ ABSORBER
NICKEL CATALYST
PROPANE HANDLING AND PURIFICATION
HYDROGEN PRODUCTION
HYDROGEN PURIFICATION

FIG. 6 APP.—Flow diagram: production of high-purity hydrogen.

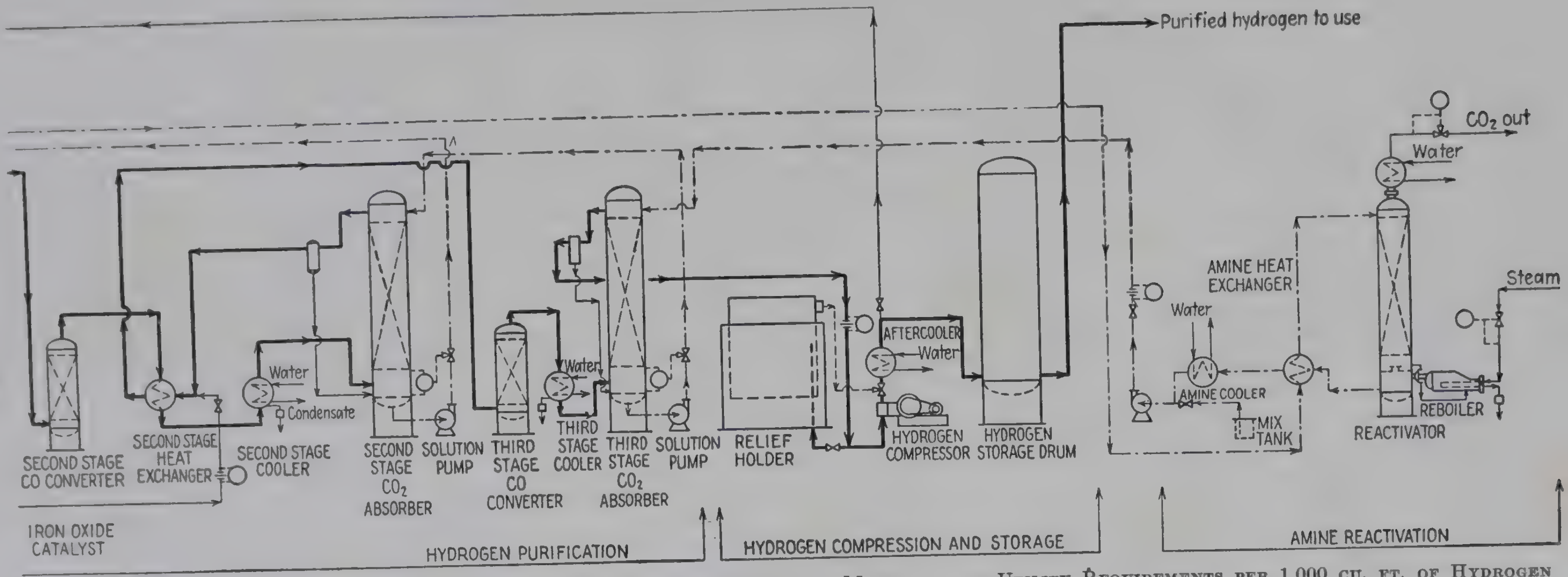
HYDROGEN*

In a typical Hygirtol plant as designed and built by the Girdler Corporation for the production of high-purity natural gas, or hydrogen from hydrocarbons and steam, propane, from a pressure storage tank flows through caustic and water scrubbers for the removal of sulfur compounds, then is mixed with steam, and passes through the hydrogen furnace where the propane and steam react at about 1500°F. over a **nickel catalyst** to produce carbon oxides and hydrogen. On the furnace outlet more steam is added to cool the gas to about 750°F., after which the mixture passes through the first-stage carbon monoxide converter where the greater part of the carbon monoxide is oxidized to carbon dioxide. Leaving the converter, the gas passes through a heat exchanger and cooler, and then enters the first-stage carbon dioxide absorber where a stream of monoethanolamine solution removes the carbon dioxide from the gas. On the absorber outlet, steam is mixed with the gas, and the mixture passes through the heat exchanger, where it is heated and then flows to the second-stage carbon monoxide converter containing an **iron oxide** catalyst for further carbon monoxide oxidation.

The purification of the hydrogen is completed by carbon dioxide removal, followed by another stage of carbon monoxide oxidation and carbon dioxide removal. The removal of carbon dioxide is effected by the same solution flowing through all three absorbers in series in reverse order to the gas flow and then being regenerated continuously by boiling and steam stripping.

The purified hydrogen is more than 99.9 per cent pure, with less than 0.01 per cent of carbon monoxide or carbon dioxide, and less than 0.1 per cent residual hydrocarbon.

APPENDIX 6 (*continued*)


Purified hydrogen to use
CO$_2$ out
Water
Steam
SECOND STAGE CO CONVERTER
SECOND STAGE HEAT EXCHANGER
Water
Condensate
SECOND STAGE COOLER
SECOND STAGE CO$_2$ ABSORBER
SOLUTION PUMP
THIRD STAGE CO CONVERTER
Water
THIRD STAGE COOLER
THIRD STAGE CO$_2$ ABSORBER
SOLUTION PUMP
RELIEF HOLDER
AFTERCOOLER
Water
HYDROGEN COMPRESSOR
HYDROGEN STORAGE DRUM
Water
AMINE HEAT EXCHANGER
AMINE COOLER
MIX TANK
REACTIVATOR
REBOILER
IRON OXIDE CATALYST
HYDROGEN PURIFICATION
HYDROGEN COMPRESSION AND STORAGE
AMINE REACTIVATION

The operation of a plant is continuous, and requires only part-time supervision by an operator. In some cases the carbon dioxide removal equipment has been housed, although outdoor installations here are in more general use.

Pure carbon dioxide is obtained as a by-product in Hygirtol plant operation. This amounts to 35 lb. of carbon dioxide per 1,000 cu. ft. of hydrogen produced. By the addition of scrubbing and compression equipment, liquid carbon dioxide may be recovered for sale or use. The carbon dioxide gas produced by the plant is also suitable for purging and blanketing operations.

* *Chem. Met. Eng.*, May, 1946.

Material and Utility Requirements per 1,000 cu. ft. of Hydrogen

Material	Quantity
Process material,	
Propane, gal.	2.75
or	
Natural gas, cu. ft.	250
Fuel (gas or oil) B.t.u.	250,000
Steam, lb.	380
Cooling water, gal. (30°F. rise)	1,600
Power, kwh.	2
Chemicals, cost in cents	2

APPENDIX 7

ALCOHOLS—PROPERTIES*

Product	Chemical formula	Molecular weight	Specific gravity 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C.	
									In water	Water in
Methanol	CH_3OH	32.04	0.7924	6.6	64.5	92.0	− 97.6	60	Complete	Complete
Ethanol (190 proof)	C_2H_5OH	......	0.8126	6.8	78.2	43.0	....	75	Complete	Complete
Ethanol (200 proof)	C_2H_5OH	46.07	0.7905	6.6	78.3	44.0	−114.4	70	Complete	Complete
Isopropanol (91 % by vol.)	$(CH_3)_2CHOH$	......	0.8179	6.8	80.4	....	− 50	70	Complete	Complete
Isopropanol	$(CH_3)_2CHOH$	60.09	0.7862	6.5	82.3	33.0	− 87.8	70	Complete	Complete
Allyl alcohol	$CH_2{:}CHCH_2OH$	58.08	0.8534	7.1	97.1	19.0	−129	90	Complete	Complete
Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	0.8109	6.7	117.7	5.5	− 90	115	7.7	20.1
Methyl amyl alcohol	$(CH_3)_2CHCH_2CH(OH)CH_3$	102.17	0.8079	6.7	131.8	3.8	....	115	1.7	5.8
Ethylbutanol	$(C_2H_5)_2CHCH_2OH$	102.17	0.8328	6.9	148.9	0.9	....	135	0.43	4.6
Hexanol	$(CH_3(CH_2)_4CH_2OH$	102.17	0.8208	6.8	157.2	0.7	− 44.6	165	0.58	7.2
Heptanol	$CH_3(CH_2)_4CH(OH)CH_3$	116.20	0.8187	6.8	160.4	0.9	....	160	0.35	5.1
Ethylhexanol	$C_4H_9CH(C_2H_5)CH_2OH$	130.22	0.8340	6.9	183.5	0.36	....	185	0.10	2.6
Undecanol	$C_4H_9CH(C_2H_5)C_2H_4CH(OH)CH_3$	172.30	0.8363	7.0	225.4	0.04	....	235	<0.02	2.1
Tetradecanol	$C_4H_9CH(C_2H_5)C_2H_4CH(OH)CH_2CH(CH_3)_2$	214.38	0.8355	7.0	264.1	0.01	....	285	<0.02	0.66
Heptadecanol	$C_4H_9CH(C_2H_5)C_2H_4CH(OH)C_2H_4CH(C_2H_5)_2$	256.46	0.8475	7.1	309.0	<0.01	....	310	<0.02	0.46
Trimethylcyclohexanol.	$\underbrace{CH(OH)CH_2C(CH_3)_2CH_2CH(CH_3)CH_2}$	132.23	$0.8777\frac{40}{20°}$	$7.3_{40°}$	198.0	$0.9_{40°}$	35.7	165	Slight	
Mercaptoethanol	$HSCH_2CH_2OH$	78.13	1.1168	9.3	157.1	1.0	....	170	Complete	Complete

* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 8

GLYCOLS AND ETHERS—PROPERTIES*

Product	Chemical formula	Molecular weight	Specific gravity, 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C	
									In water	Water in
Ethylene glycol	$HOCH_2CH_2OH$	62.07	1.1155	9.3	197.2	0.12	-13.0	240	Complete	Complete
Diethylene glycol	$HOC_2H_4OC_2H_4OH$	106.12	1.1184	9.3	245.0	0.01	-8.0	290	Complete	Complete
Triethylene glycol	$HOC_2H_4OC_2H_4OC_2H_4OH$	150.17	1.1254	9.4	287.4	<0.01	-7.2	330	Complete	Complete
Propylene glycol	$CH_3CHOHCH_2OH$	76.09	1.0381	8.6	188.2	0.07	....	225	Complete	Complete
Dipropylene glycol	$(CH_3CHOHCH_2)_2O$	134.17	1.0252	8.5	231.8	0.01	....	280	Complete	Complete
1, 3-Butylene glycol	$C_4H_8(OH)_2$	90.12	1.0059	8.4	207.5	0.06	....	.....	Complete	Complete
Ethylhexanediol	$C_3H_7CH(OH)CH(C_2H_5)CH_2OH$	146.22	0.9422	7.8	244.2	<0.01	-40.0	260	4.2	11.7
Ethyl ether	$C_2H_5OC_2H_5$	74.12	0.7146	5.9	34.5	442.0	-116.3	-40	6.9	1.3
Isopropyl ether	$(CH_3)_2CHOCH(CH_3)_2$	102.17	0.7244	6.0	68.5	119.0	-85.5	15	1.90	0.57
Butyl ether	$C_4H_9OC_4H_9$	130.22	0.7694	6.4	142.2	4.8	-95.2	100	0.03	0.19
Hexyl ether	$C_6H_{13}OC_6H_{13}$	186.33	0.7942	6.6	226.2	0.07	-43.0	170	<0.01	0.12
Dichlorethyl ether	$ClCH_2CH_2OCH_2CH_2Cl$	143.02	1.2220	10.2	178.5	0.7	-51.9	185	1.1	0.28
Triglycol dichloride	$Cl(CH_2CH_2O)_2C_2H_4Cl$	187.07	1.1974	10.0	241.3	0.03	-31.5	250	1.9	0.83
Dichlorisopropyl ether	$[ClCH_2(CH_3)CH]_2O$	171.07	1.1135	9.3	187.4	0.1	....	185	0.17	0.14
Ethylene oxide	$(CH_2)_2{:}O$	44.05	0.8711	7.2	10.7	1095.0	-111.0	<0	Complete	Complete
Propylene oxide	$CH_3CH\underbrace{CH_2O}$	58.08	0.8304	6.9	33.9	445.0	-104.4	-35	40.5	12.8
Dioxane	$O{:}(CH_2CH_2)_2{:}O$	88.10	1.0356	8.6	101.3	29.0	11.8	65	Complete	Complete

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* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 9

ESTERS—PROPERTIES*

Product	Chemical formula	Molecular weight	Specific gravity, 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C.	
									In water	Water in
Ethyl acetate........	$CH_3COOC_2H_5$	88.10	0.9018	7.5	77.1	65.0	−83.5	40	8.7	3.3
Isopropyl acetate....	$CH_3COOCH(CH_3)_2$	102.13	0.8737	7.3	88.4	47.5	−69.3	60	2.9	1.8
Butyl acetate........	$CH_3COOC_4H_9$	116.16	0.8826	7.3	126.3	8.7	−75	100	0.68	1.2
Methyl amyl acetate.	$CH_3COOCH(CH_3)CH_2CH(CH_3)_2$	144.21	0.8595	7.1	146.3	3.8	−63.8	110	0.13	0.58
Ethylbutyl acetate...	$CH_3COOCH_2CH(C_2H_5)_2$	144.21	0.8803	7.3	162.4	1.8	......	130	$0.06_{25°}$	0.57
Ethylhexyl acetate...	$CH_3COOCH_2CH(C_2H_5)C_4H_9$	172.26	0.8734	7.3	198.6	0.40	......	190	<0.03	0.55
Glycol diacetate.....	$CH_3COOCH_2CH_2OCOCH_3$	146.14	1.1063	9.2	190.5	0.3	−41.5	220	16.4	7.0
Glycol diformate....	$HCOOCH_2CH_2OCOH$	118.09	1.2277	10.2	177.1	0.5	−10	200	Decomp.	Decomp.
Diethyl sulfate......	$(C_2H_5)_2SO_4$	154.18	1.1803	9.8	Decomp.	0.19	−24.4	250	0.7	0.3
Ethyl silicate........	$(C_2H_5)_4SiO_4$	208.30	0.9356	7.8	168.1	1.0	−77	125	Decomp.	Decomp.
Methyl acetoacetate.	$CH_3COCH_2COOCH_3$	116.11	1.0785	9.0	171.7	0.7	−31.9	170	44.5	19.8
Ethyl acetoacetate...	$CH_3COCH_2COOC_2H_5$	130.14	1.0261	8.5	180.7	0.8	−43.3	185	11.6	4.9
Butyl acetoacetate...	$CH_3COCH_2COOC_4H_9$	158.19	0.9694	8.1	213.9	0.19	−35.6	185	0.40	2.8

* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 10

ACIDS AND ANHYDRIDES—PROPERTIES*

Product	Chemical formula	Molecular weight	Specific gravity, 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C	
									In water	Water in
Acetic acid	CH_3COOH	60.05	1.0510	8.7	118.0	11.7	16.6	135	Complete	Complete
Butyric acid	$CH_3CH_2CH_2COOH$	88.10	0.9590	7.8	163.7	0.8	-6.3	170	Complete	Complete
Ethylbutyric acid	$(C_2H_5)_2CHCOOH$	116.16	0.9225	7.7	194.0	0.08	-9.4	210	0.22	3.3
Caproic acid	$CH_3CH_2CH_2CH_2CH_2COOH$	116.16	0.9295	7.7	205.1	0.18	-5.4	215	1.1	5.4
Ethylhexoic acid	$C_4H_9CH(C_2H_5)COOH$	144.21	0.9077	7.6	226.9	0.03	-118.4	260	0.25	1.23
Acetic anhydride	$(CH_3CO)_2O$	102.09	1.0830	9.0	139.9	4.1	-67.7	150	Decomp.	Decomp.
Propionic anhydride	$(CH_3CH_2CO)_2O$	130.14	1.0119	8.4	169.0	1.0	-43	165	Decomp.	Decomp.
Butyric anhydride	$(CH_3CH_2CH_2CO)_2O$	158.19	0.9681	8.1	199.5	0.3	-65.1	190	Decomp.	Decomp.
Maleic anhydride	$(COCH{:}CHCO){:}O$	98.06	$1.305\,\frac{60}{20^\circ}$	10.9_{60°	202.0	.....	52.6	240	Decomp.	Decomp.

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* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 11

KETONES AND ALDEHYDES—PROPERTIES*

Product	Chemical formula	Molecular weight	Specific gravity, 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C.	
									In water	Water in
Acetone	CH_3COCH_3	58.08	0.7910	6.6	56.1	178.0	−95.1	15	Complete	Complete
Methyl isobutyl ketone	$(CH_3)_2CHCH_2COCH_3$	100.16	0.8042	6.7	115.8	15.7	−80.4	75	2.0	2.2
Methyl amyl ketone	$CH_3CO(CH_2)_4CH_3$	114.18	0.8166	6.8	150.6	2.6	−26.9	120	0.43	1.5
Diacetone alcohol	$(CH_3)_2COHCH_2COCH_3$	116.16	0.9406	7.8	169.1	1.1	−42.8	155	Complete	Complete
Mesityl oxide	$(CH_3)_2C{:}CHCOCH_3$	98.14	0.8569	7.1	128.0	8.7	−46.4	90	2.8	3.4
Isophorone	$COCH{:}C(CH_3)CH_2C(CH_3)_2CH_2$	138.20	0.9229	7.7	215.2	0.3	− 8.1	205	1.2	4.3
Acetonylacetone	$CH_3COCH_2CH_2COCH_3$	114.14	0.9734	8.1	192.2	0.43	− 5.4	180	Complete	Complete
Pentanedione-2, 4	$CH_3COCH_2COCH_3$	100.11	0.9753	8.1	140.5	7.0	−23.5	105	16.6	5.4
Butyraldehyde	$CH_3CH_2CH_2CHO$	72.10	0.8048	6.7	75.7	91.5	−99.0	20	7.1	3.2
Ethylbutyraldehyde	$(C_2H_5)_2CHCHO$	100.16	0.8164	6.8	116.8	13.7	−89.0	70	0.4	0.8
Ethylhexaldehyde	$C_4H_9CH(C_2H_5)CHO$	128.21	0.8205	6.8	163.4	1.8	......	125	<0.02	0.4
2-Ethyl-3-propylacrolein	$C_3H_7CH{:}C(C_2H_5)CHO$	126.19	0.8518	7.1	175.0	1.0	......	155	0.07	0.65
Glyoxal	$(CHO)_2$	58.04	1.26	10.0	.....	......	......	...	Complete	Complete

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* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 12

AMINO COMPOUNDS—PROPERTIES

Product	Chemical formula	Molecular weight	Specific gravity, 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C.	
									In water	Water in
Butylamine	$C_4H_9NH_2$	73.14	0.7385	6.1	77.1	72.0	−49.2	45	Complete	Complete
Ethylenediamine	$NH_2C_2H_4NH_2$	60.10	0.8995	7.5	117.2	10.7	10.8	110	Complete	Complete
Diethylenetriamine	$NH_2C_2H_4NHC_2H_4NH_2$	103.17	0.9542	7.9	206.7	0.2	......	215	Complete	Complete
Triethylenetetramine	$NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$	146.24	0.9818	8.2	277.5	<0.01	......	290	Complete	Complete
Propylenediamine	$CH_3CH(NH_2)CH_2NH_2$	74.13	0.8732	7.3	119.7	9.4	......	120	Complete	Complete
Morpholine	$O:(CH_2CH_2)_2:NH$	87.12	1.0017	8.3	128.6	8.0	− 3.1	100	Complete	Complete
Methyl morpholine	$C_2H_4OC_2H_4NCH_3$	101.15	0.921	7.7	115.4	....	......	...	Complete	Complete
Ethyl morpholine	$CH_2CH_2OC_2H_4NCH_2CH_3$	115.17	0.916	7.6	138.0	16.0	......	89.6	Complete	Complete
Aminoethyl morpholine	$C_2H_4OC_2H_4NC_2H_4NH_2$	130.19	1.000	8.3	202.0	....	......	.....	Complete	Complete
Monoethanolamine	$HOCH_2CH_2NH_2$	61.08	1.0179	8.5	170.5	0.4	10.5	200	Complete	Complete
Diethanolamine	$(HOCH_2CH_2)_2NH$	105.14	$1.0920_{\frac{30}{20°}}$	$9.1_{30°}$	269.1	<0.01	28.0	305	95.4	
Triethanolamine	$(HOCH_2CH_2)_3N$	149.19	1.1258	9.4	360	<0.01	21.2	380	Complete	Complete
Dimethylethanolamine	$(CH_3)_2NC_2H_4OH$	89.14	0.887	7.4	133.5	10.0	......	88	Complete	Complete
Methyldiethanolamine	$CH_3N(C_2H_4OH)_2$	119.16	1.0418	8.7	247.2	<0.01	−21.0	260	Complete	Complete
Diethylethanolamine	$(C_2H_5)_2NC_2H_4OH$	117.19	0.8851	7.4	162.1	1.4	......	140	Complete	Complete
Aminoethylethanolamine	$NH_2C_2H_4NHC_2H_4OH$	104.15	1.0304	8.6	243.7	0.01	......	275	Complete	Complete
Isopropanolamine	$CH_3CH(OH)CH_2NH_2$	75.11	0.9619	8.0	159.9	0.6	1.4	160	Complete	Complete
Diisopropanolamine	$(CH_3CH(OH)CH_2)_2NH$	133.19	$0.9890_{\frac{45}{20°}}$	$8.2_{45°}$	248.7	$0.02_{42°}$	42.0	260	87	
Triisopropanolamine	$[CH_3CH(OH)CH_2]_3N$	191.27	0.9996	$8.3_{60°}$	305.0	<0.01	58.0	320		

* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 13

CHLORINE COMPOUNDS—PROPERTIES

Product	Chemical formula	Molecular weight	Specific gravity, 20/20°C.	Lb. per gal. at 20°C.	Boiling point, °C., 760 mm.	Vapor pressure, mm. Hg at 20°C.	Freezing point, °C.	Flash point, °F.	Solubility, % by weight at 20°C.	
									In water	Water in
Ethylene dichloride..	$ClCH_2CH_2Cl$	98.97	1.2554	10.4	83.5	62.0	− 35.5	70	0.81	0.15
Propylene dichloride.	$CH_3CHClCH_2Cl$	112.99	1.1583	9.6	96.3	40.0	....	70	0.26	0.06
Trichlorethane......	$ClCH_2CHCl_2$	133.42	1.4432	12.0	113.7	16.7	− 36.4	Non Flammable	0.45	0.05
Butyl chloride.......	$CH_3CH_2CH_2CH_2Cl$	92.57	0.8875	7.4	78.6	80.1	−122.8	15	0.11	0.8
Dichlorethyl formal..	$CH_2(OCH_2CH_2Cl)_2$	173.04	1.2339	10.3	218.1	0.1	− 32.8	230	0.78	0.44
Ethylene chlorhydrin.	$ClCH_2CH_2OH$	80.52	1.2045	10.0	128.7	4.9	− 62.6	140	Complete	Complete
Propylene chlorhydrin..............	$CH_3CHOHCH_2Cl$	94.54	1.1128	9.3	127.4	4.9	....	125	Complete	Complete
Dichlorethyl ether...	$ClCH_2CH_2OCH_2CH_2Cl$	143.02	1.2220	10.17	178.5	0.7	− 51.9	185	1.1	0.28
Dichlorisopropyl ether............	$[ClCH_2(CH_3)CH]_2O$	171.07	1.1135	9.27	187.4	0.1	....	185	0.17	0.14
Triglycol dichloride..	$ClC_2H_4OC_2H_4OC_2H_4Cl$	187.07	1.1974	9.96	241.3	0.03	− 31.5	250	1.9	0.83

* Courtesy of Carbide and Carbon Chemical Corp.

APPENDIX 14

CHEMICAL END-USE PATTERNS

Information pertaining to the ultimate uses of chemicals produced by organic synthesis is frequently of no less importance than knowledge of the methods of their preparation. End-use patterns of some of the more important organic chemicals, along with *approximate* figures regarding their principal end uses, are presented below. In general the indicated total consumption figures will reflect closely the statistics reported for the year 1946 by the Tariff Commission. No effort, however, was made to introduce exact data because it is known that (1) strikes and reconversion problems affected production; (2) wartime restrictions and shortages markedly affected distribution patterns; and (3) the future end-use pattern will be significantly affected by the satiation of certain markets, the introduction of new materials, and changes in the competitive economics of old and new products and processes. In arriving at the end-use estimates, use was made of (1) similar wartime data reported by the Bureau of the Census; (2) prewar and current production figures issued by the Tariff Commission; (3) the monthly report on chemicals by the Bureau of Foreign and Domestic Commerce; and (4) the appreciated advice and cooperation of men in government and industry.

BENZENE END-USE PATTERN
(In thousands of gallons)

Uses	Approximate	
	Amount	Per cent
Styrene for rubber	42,000	28.4
Phenol	28,000	18.9
Miscellaneous[1]	20,900	14.1
Styrene for plastics	15,000	10.1
Aniline	12,000	8.1
Solvents	10,000	6.8
Chlorobenzene[2]	6,000	4.0
Nitrobenzene	5,000	3.4
Dichlorobenzenes	3,000	2.0
Maleic anhydride	2,000	1.4
Diphenyl	2,000	1.4
Medicinals	1,000	.7
Rubber chemicals	600	.4
Anthraquinones	300	.2
Trichlorobenzene	200	.1
Approximate total consumption[3]	148,000	100.0

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[1] Includes use in manufacture of nylon, phthalate plasticizers, camphor, resorcinol, alcohol denaturants, quantity for nylon via cyclohexane and cyclohexanol is substantial part of total.

[2] Largely for manufacture of D.D.T.

[3] Does not include motor grade "benzol."

PHENOL END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Phenolic resins	110,000	61.1
Chemical manufacture[1]	18,000	10.0
Salicylates	12,000	6.6
Petroleum refining[2]	10,000	5.6
Disinfectants and insecticides[3]	10,000	5.6
Trephenyl phosphate and other plasticizers	8,500	4.7
Toluene extraction	3,000	1.6
Dyes and inks	1,800	1.0
Medicinals, other than salicylates	1,700	1.0
Miscellaneous uses and exports	5,000	2.8
Approximate total consumption[4]	180,000	100.0

[1] Includes substituted phenols such as dichloro- and butylphenol.
[2] Includes phenol in oil additives and oil refining materials.
[3] Includes chlorinated phenols.
[4] Includes synthetic and natural; technical and U.S.P.

ANILINE END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Rubber chemicals[1]	30,000	39.5
Dyestuffs, pigments, intermediates	28,000	36.8
Drugs and pharmaceuticals[2]	4,000	5.3
Explosives and stabilizers	3,000	3.9
Photographic chemicals	1,800	2.4
Petroleum refining[3]	1,500	2.0
Resins and plastics	2,700	3.5
Miscellaneous uses[4]	5,000	6.6
Approximate total consumption	76,000	100.0

[1] Synthetic rubber additives such as diphenylamine, cyclohexylamine, and hydroquinone.
[2] Sulfa drugs.
[3] Emulsion breakers, petroleum additives.
[4] Flotation products, paraciticides, mildew inhibiters, exports, etc.

NAPHTHALENE END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Phthalic anhydride	145,000	55.8
Other intermediates[1]	60,000	23.1
Moth repellents and insecticides[2]	35,000	13.5
Miscellaneous uses[3]	20,000	7.6
Approximate total consumption[4]	260,000	100.0

[1] Includes mostly refined naphthalene to manufacture beta naphtol, chlorinated naphthalene, naphthalenesulfonic acids, and other intermediates.

[2] Includes agricultural insecticides.

[3] Includes oil additives and oil treating agents and other primary products.

[4] Includes approximately 175 million pounds crude solidifying at less than 79° C., 85 million pounds solidifying at or over 79° C.

PHTHALIC ANHYDRIDE END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Esters (plasticizers)[1]	50,000	45.2
Resins, principally alkyd	45,000	40.8
Dyestuffs	12,000	10.8
Food and drugs[2]	2,500	2.3
Petroleum additives (principally demulsifying agents)	500	.4
Chemical intermediates	350	.3
Rubber chemicals (principally vulcanization agents)	100	.1
Miscellaneous[3]	150	.1
Approximate total consumption	110,600	100.0

[1] Largely dibutyl and dioctyl phthalates but includes some ethyl and amyl esters.

[2] Includes use for benzoic acid.

[3] Includes use in paints, lacquers, enamels, and resin softeners.

Methanol End-use Pattern
(In thousands of gallons)

Uses	Approximate	
	Amount	Per cent
Chemicals	47,000	
Formaldehyde[1]	36,000	44.0
Ethylene glycol and brake fluid	6,000	7.3
Acetic acid	1,500	1.8
Dimethylaniline and methylamines	1,000	1.2
Methyl formate, formamide	600	.7
Other chemicals[2]	1,900	2.3
Other uses	35,000	
Antifreeze	25,000	30.5
Plastics[3]	3,000	3.7
Denaturants[4]	2,000	2.4
Solvents	1,000	1.2
Drugs and pharmaceuticals	1,000	1.2
Photographic materials and printing inks	1,000	1.2
Natural and synthetic rubber; processing	400	.5
Miscellaneous uses[5]	1,600	2.0
Approximate total consumption	82,000	100.0

[1] Some formaldehyde produced by oxidation of natural gas.

[2] Includes methyl acetate, methyl bromide, other methyl esters, and dyestuffs.

[3] Includes use in preparation of, or processing methyl methacrylate, polyvinyl alcohol, vinyl plastics, nylon.

[4] Wood alcohol (natural methanol) used for this purpose.

[5] Includes use preparation of lacquers, varnishes, polishing preparations, adhesives, and petroleum products.

FORMALDEHYDE END-USE PATTERN

(In thousands of pounds: basis 37% by weight)

Uses	Approximate	
	Amount	Per cent
Resins, total	270,000	
Phenolic	150,000	32.0
Urea and melamine	115,000	24.5
Other resins[1]	5,000	1.0
Chemicals, total	160,000	
Hexamethylene tetramine	50,000	10.6
Pentaerythritol	28,000	6.0
Rubber chemicals	2,000	.4
Other chemicals[2]	80,000	16.0
Other Uses	40,000	
Textiles	8,500	1.9
Dyes and intermediates	4,500	.9
Leather	2,500	.5
Embalming fluid	1,200	.2
Drugs and pharmaceuticals[3]	800	.1
Paper	600	.1
Adhesives and protective coatings	600	.1
Disinfectants and insecticides[4]	500	.1
Photography	400	.1
Miscellaneous uses[5]	8,400	1.9
Exports	12,000	2.6
Approximate total consumption	470,000	100.0

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[1] Includes formaldehyde used in manufacture of synthetic resins such as polyvinyl, casein, cashew, phthalic alkyd, dimethylurea.

[2] Includes use for manufacture of ethylene glycol, paraformaldehyde, hydroxyacetic (glycolic) acid, citric acid, methoxy-methoxyl-ethanol, and methyl-hydroxyacetate.

[3] Roughly half of this quantity for processing penicillin.

[4] Includes germicides and fungicides.

[5] Includes use for manufacture of theobromine, explosives, boiler and metal treating compounds.

DENATURED ETHYL ALCOHOL END-USE PATTERN
(Thousands of wine gallons = 190 proof)

Uses[1]	Approximate	
	Amount	Per cent
Chemical manufacture	95,000	
Acetaldehyde and acetic acid	70,000	40.8
Ethyl acetate	8,000	4.7
Ethers	2,500	1.5
Basic medicinal chemicals	2,000	1.2
Other ethyl esters	2,500	1.5
Other chemicals[2]	10,000	5.8
Solvent uses	43,000	
Nitrocellulose lacquers	5,000	2.9
Shellac and resins	9,000	5.3
Pharmaceuticals and cosmetics	6,000	3.4
Adhesives and coatings	2,000	1.1
Inks and duplicating equipment	1,000	.5
General solvents	20,000	11.7
Other uses	33,500	
Antifreeze	20,000	11.7
Vinegar and foods[3]	8,500	5.0
Miscellaneous uses[4]	5,000	2.9
Approximate total consumption[5]	171,500	100.0

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[1] Prewar annual use was about 120 million gallons. During the war (1944–45) about 1 million gallons of alcohol was used daily in synthetic rubber program to produce butadiene; this is now based on butenes and butane. The 1946 production was closely 173 million gallons.

[2] Includes ethanol for tetraethyl lead, chloral, and D.D.T.

[3] For vinegar, mold preservatives, flavoring extracts, food products, and candy glazes.

[4] Purification of plasticizers and plastics, and textile processing.

[5] About half made from ethylene via mixture of mono- and diethyl sulfates.

ETHYLENE GLYCOL END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Antifreeze and coolants	140,000	71.8
Explosives	9,000	4.6
Cellophane	8,000	4.1
Chemicals and synthetic resins	12,000	6.2
Hydraulic brake fluids	6,000	3.1
Radio condenser fluid	800	.4
Textiles and rayon	3,000	1.5
Miscellaneous uses	10,000	5.1
Exports	6,200	3.2
Approximate total consumption	195,000	100.0

ISOPROPANOL END-USE PATTERN
(In thousands of gallons)

Uses	Approximate	
	Amount	Per cent
Chemical uses	62,500	
Acetone	52,000	60.5
Isopropyl acetate, xanthates, etc	10,500	12.2
Technical uses	23,500	
Antifreeze and deicing	7,000	8.1
Coatings, plastics and resins	4,500	5.2
Drugs, cosmetics, rubbing alcohol	4,100	4.8
Solvents, cleaners, blends	3,500	4.1
Textile processing	600	.7
Pectin and zein	500	.6
Gasoline antioxidants, brake fluids	850	1.0
Disinfectants and germicides	250	.2
Miscellaneous uses	2,200	2.6
Approximate total consumption	86,000	100.0

ACETONE END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Cellulose acetate and other textiles including manufacture of ketene[1]	163,000	48.5
Chemical manufacture	63,000	18.8
Acetylene (solvent)	14,000	4.2
Solvents	12,000	3.6
Plastics	14,000	4.2
Rubber	10,000	2.9
Miscellaneous uses	60,000	17.8
Approximate total consumption	336,000	100.0

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[1] Used largely for the production of ketene $CH_2{:}CO$, which reacts with acetic acid to give acetic anhydride and with ethanol to give ethyl acetate.

NORMAL-BUTYL ALCOHOL END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Chemical manufacture	75,000	
Butyl acetate	38,000	33.0
Dibutyl phthalate	12,000	10.4
Other butyl derivatives[1]	25,000	21.7
Lacquer Solvents	15,000	
Protective coatings[2]	10,000	8.7
Textiles and leather	3,000	2.6
Dyes and penetrants	2,000	1.7
Other uses	25,000	
Resins and plastics	8,000	7.1
Photography and films	1,500	1.3
Hydraulic brake fluids	1,500	1.3
Oil additives	1,500	1.3
Miscellaneous uses[3]	12,500	10.9
Approximate total consumption	115,000	100.0

[1] Includes butanol used for butyl cellosolve and butylamines.

[2] Coating compositions for motor and other heavy industries.

[3] Includes butanol to make cellulose acetate sheets, insect repellents, medicinals, flotation reagents, butyric acid, and dehydrating agents.

ACETIC ACID END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Plastics and resins[1]	180,000	34.0
Acetic anhydride[2]	160,000	30.1
Organic acetates[3]	100,000	18.9
Textile processing	27,000	5.1
Metallic acetates[4]	5,500	1.
Drugs and pharmaceuticals	16,000	3.
Paints and pigments	5,000	1.
Rubber chemicals	2,000	.4
Photography	5,500	1.
Miscellaneous uses	29,000	5.5
Approximate total consumption[5]	530,000	100.0

[1] Principally vinyl resins.

[2] Recovered acid concentrated by vapor-phase process.

[3] Such as ethyl, butyl, amyl acetates.

[4] Mostly sodium and aluminum salts.

[5] Comprises about 281 and 29 million pounds of synthetic and natural acetic acids, respectively, and 210 million pounds (out of 1,188 million pounds) recovered acetic acid from acetate fiber operations.

ACETIC ANHYDRIDE END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Yarns and fibers	360,000	69.2
Plastics and resins	130,000	25.0
Drugs and pharmaceuticals[1]	10,000	1.9
Perfumes and flavor bases	5,000	1.0
Textile processings and dyeing	5,000	1.0
Miscellaneous uses[2]	10,000	1.9
Approximate total consumption[3]	520,000	100.0

[1] Approximately 60 per cent for aspirin.

[2] Includes diacetin and triacetin.

[3] Produced from ketene, acetylene, ethylene, and acetic acid by the vapor-phase process.

CARBON TETRACHLORIDE END-USE PATTERN
(In thousands of pounds)

Uses	Approximate	
	Amount	Per cent
Fire extinguishers	70,000	46.7
Degreasing compounds	32,000	21.3
Dry cleaning	18,000	12.0
Agriculture[1]	5,000	3.3
Drugs	3,500	2.3
Synthetic rubber	3,000	2.
Miscellaneous uses	16,000	10.7
Exports	2,500	1.7
Approximate total consumption	150,000	100.0

[1] Principally for grain fumigants.

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[1] The spelling of names and the style of indexing are according to the policy of *Chemical Abstracts*.

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